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ON CERTAIN ADDITION-COMPOUNDS DERIVED FROM ORTHOBENZOQUINONE.[1]

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The work described in this paper was suggested by the discovery[2] of the aniline, ethyl alcohol, and methyl alcohol addition-compounds from dianilinodibromorthobenzoquinone, for it seemed probable that tetrabromorthobenzoquinone would also show a tendency to form addition-compounds, especially as the formation of such compounds from other orthoquinones had been observed previously by Zincke and Arnst,[3] Zincke and Neumann,[4] and Zincke and Schaum[5] with alcohols or water, by Japp[6] with ketones, and by Klinger[7] with acetaldehyde. Zincke,[8] too, in his work on tetrabromorthobenzoquinone had noticed that glacial acetic acid, or a mixture of ether and ligroin, gave a white compound with it, and

[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by Horace C. Porter.

[2] This JOURNAL, **30**, 518 (1903).

[3] Ann. Chem. (Liebig), **267**, 319 (1892).

[4] *Ibid.*, **278**, 173 (1894).

[5] Ber. d. chem. Ges., **27**, 537 (1894).

[6] *Ibid.*, **17**, 2826 (1884); J. Chem. Soc. (London), **78**, 1034 (1899).

[7] Ann. Chem. (Liebig), **249**, 138 (1888).

[8] Ber. d. chem. Ges., **20**, 1776 (1887).

Koch and one of us[1] had prepared the puzzling white acetic acid product, but had made little progress toward settling its nature.

Our first experiments in this direction showed that the tetrabromorthobenzoquinone has a very strong tendency to combine with substances belonging to various classes and we selected for especial study at first its compounds with alcohols and with water. These bodies were obtained by allowing the solid tetrabromorthoquinone to stand with the substance at ordinary temperatures for some days or weeks (in the case of water moist toluol or benzol was used). The products are composed of 2 molecules of tetrabromorthobenzoquinone combined with one of the other substance. They are all white, crystallize in needles or prisms, and, although stable at ordinary temperatures and on crystallization from many solvents, are decomposed by heat, yielding as the principal decomposition-product the red hexabromorthoquinopyrocatechin ether, $C_6Br_4{=}O_2{=}C_6Br_2O_2$. This reaction in most cases runs quantitatively, thus:

$$(C_6Br_4O_2)_2CH_3OH = C_6Br_4O_2C_6Br_2O_2 + CH_3OH + Br_2.$$

This strong similarity in properties has led us to class them together, and to call them α-compounds. We have prepared the following members of this series:

α-Series.

Compound.	Melting-point.
$(C_6Br_4O_2)_2.H_2O$	190°–200°
$(C_6Br_4O_2)_2CH_3OH$	175°–185°
$(C_6Br_4O_2)_2C_7H_7OH$	165°–170°
$(C_6Br_4O_2)_2CH_3COOH$	220°–230°

The so-called melting-points are really decomposition-points, as the substances are entirely converted into the red pyrocatechin ether at these temperatures; consequently these points are much affected by the length of heating and other conditions, so that it is not worth while to try to fix them more definitely.

From the α-compounds a second series of isomeric bodies

[1] This JOURNAL, **26**, 42 (1901).

was obtained—the methyl compound by boiling the α-body with methyl alcohol, while the water and benzyl alcohol bodies, which could not be formed in this way, were made by the regulated action of acetic anhydride and dry sodic acetate on the α-compounds. All the compounds of the second series, which we designate with β, form white polygonal plates, melt at definite points without decomposition, and are remarkably stable toward heat, solvents, and many reagents. The following substances have been prepared:

β-Series.

Compound.	Melting-point.
$(C_6Br_4O_2)_2CH_3OH$	261°
$(C_6Br_4O_2)_2C_7H_7OH$	216°
$(C_6Br_4O_2)_2H_2O$	222°

The water substance was not analyzed, and is classed here only on the strength of its properties and mode of formation. The white acetic acid compound of Koch and one of us[1] seems to be related to these substances, although not belonging strictly in this series.

All these bodies, of whichever series, are much more stable than the compounds[2] previously discovered by us,

$$C_6Br_2(C_6H_5NH)_2O_2CH_3OH,$$
$$C_6Br_2(C_6H_5NH)_2O_2C_2H_5OH,$$

and $$C_6Br_2(C_6H_5NH)_2O_2C_6H_5NH_2,$$

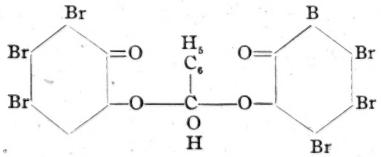
which evidently belong to a third series of addition-compounds, and are probably hemiacetals.

The three classes of addition-compounds just described do not include all those which can be formed from orthobenzoquinones, as two other different methods of addition have been observed by us already. The first product of the action of methyl alcohol on tetrabromorthobenzoquinone is a red compound melting at 192° to 193°, and giving results, on analysis, agreeing with $(C_6Br_4O_2)_3CH_3OH$, but much more work is needed before even the formula of this body can be considered established. Further, toluol and acetophenone combine with tetra-

[1] This JOURNAL, **26**, 42 (1901).
[2] *Ibid.*, **30**, 527 (1903).

bromorthobenzoquinone, giving red substances, $C_6Br_4O_2C_7H_8$ and $C_6Br_4O_3C_6H_5COCH_3$, which behave as if they were the quinone with toluol or acetophenone of crystallization, as they lose the volatile constituent by mere exposure to the air, leaving the tetrabromorthoquinone.

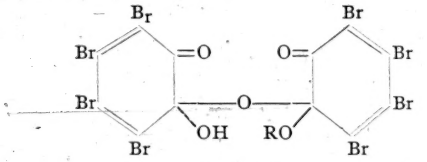
In working out the constitution of the α-addition-compounds, $(C_6Br_4O_2)_2ROH$, the most important point is to determine the way in which the two benzol rings are united. The union of carbon with carbon need not be considered, whether it is that of two atoms in the two benzol rings to form a diphenyl compound, or one in which the carbon of the added compound takes part, since a substance formed in this way would be too stable to fall easily into the hexabromorthoquinopyrocatechin ether, and this is the most striking property of the α-compounds. The union of the two quinone molecules must therefore take place through the atoms of oxygen, either by means of the quinone oxygen alone or the added substance may form a link in the connecting chain. In the latter case the most probable formula for the benzyl alcohol compound, for instance, would be this,



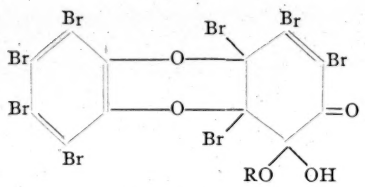
but this must be rejected for three reasons. (1) The water compound in this case would be entirely different from the alcohol compounds, whereas in fact they show the strongest similarity. (2) No satisfactory formula for the β-compounds can be worked out from this. (3) On decomposition with sulphuric acid this substance should give benzoic acid, or with hydrobromic acid, the tribromide, $C_6H_5CBr_3$, which would be easily converted into benzoic acid, but no trace of benzoic acid could be detected in the products from these reactions. The union of quinone atoms of oxygen with the oxygen of the added compound giving a chain of 3 atoms of oxygen is

so improbable, and would give such an unstable product, that it may be rejected without discussion.

The foregoing considerations leave only two possible formulas for these bodies:



Formula I.



Formula II.

When this paper was written we thought that the analyses of the reduction-product and acet-reduction-product of the α-benzyl alcohol compound proved that Formula I. was correct. Subsequent work in this laboratory has thrown doubt on our interpretation of these analytical results, and therefore the determination of the true formula of the α-compounds must be postponed until a later paper. We have retained provisionally in the body of this paper the names of the compounds according to Formula I. so as to have names under which they can be indexed.

The properties and behavior of these bodies, as observed by us, are in harmony with both of these formulas. The white color is explained by the fact that the substances are no longer quinones, but oxides, corresponding to hemiacetals, and hemiacetals are usually colorless. The easy decomposition by heat into hexabromorthoquinopyrocatechin ether, bromine, and the alcohol (or water) would take place

as follows, if Formula I. is correct: The substance is first decomposed into 2 molecules of the tetrabromorthoquinone and the added compound, then the further action of the heat converts the orthoquinone into the pyrocatechin ether with evolution of bromine. That this is the effect of heat on tetrabromorthobenzoquinone was shown by a special experiment, in which it was heated to 130° to 150°, and in this way changed into hexabromorthoquinopyrocatechin ether with evolution of bromine. The reaction, however, did not run so smoothly as the similar decomposition of the α-bodies, since some other non-volatile product beside the pyrocatechin ether was formed. This difference can be easily explained by the part which the alcohol or water of the addition-compound would take in the reaction, since it would undoubtedly reduce some of the tetrabromorthoquinone to tetrabrompyrocatechin, which would make the formation of the ether neater and more complete.

When heated with hydrobromic acid the benzyl alcohol compound gives bromine, benzal, and possibly benzyl bromide and tetrabrompyrocatechin. Here the α-body has evidently split into benzyl alcohol or bromide and a quinone, which then oxidizes part of the hydrobromic acid, the free bromine converting the original benzyl bromide, in part at least, into benzal bromide. Hydrochloric acid acts in a similar way, but the action is complicated by the substitution of bromine by the free chlorine. With the methyl alcohol compound hydrochloric acid gave chloroform, but, as there was much free chlorine present, this is of no value in determining the constitution.

Sulphuric acid of sp. gr. 1.38 gave, with the benzyl alcohol compound as the principal product, the red hexabromorthoquinopyrocatechin ether, which, if Formula I. is correct, was undoubtedly formed by the action of 2 molecules of tetrabromorthoquinone on each other, after they had been set free by the action of the acid. The conversion of the α-bodies by aniline in hot benzol into the dianilinobromparaquinoneanil can be explained in the same way.

The solubility of all these compounds in sodic hydrate would

naturally follow from the presence of a hydroxyl group in the molecule. Finally, the formation of the β- from the α-bodies can be explained by a series of natural reactions, which, however, it is not worth while to discuss until the structure of the α-bodies has been settled.

The β-methyl alcohol compound is made from the α-body by warming it with methyl alcohol; the β-benzyl alcohol or water compound is made by the regulated action of acetic anhydride on the corresponding α-substance.[1] They are so stable that they resist the action of most reagents. Almost the only positive observation made with them is that the methyl alcohol body contains a hydroxyl group, as it gives a monoacetyl derivative.

The white compound obtained by Koch and one of us[2] by evaporating glacial acetic acid over tetrabromorthoquinone is apparently related to the β-series, because it is formed from the α-body, first described in this paper, by heating it with acetic acid after the analogy of the methyl alcohol compounds, and also because of its unusual stability.

Tetrabromorthobenzoquinone gave white, or nearly white, compounds with substances belonging to the most various classes, but, since our work with toluol and benzol has shown that it has a remarkable attraction for water, we prefer to postpone all account of these experiments until they have been repeated with scrupulously dried materials.

EXPERIMENTAL PART.

Action of Methyl Alcohol on Tetrabromorthobenzoquinone.

The tetrabromorthobenzoquinone ($C_6Br_4O_2$) used in this work was prepared by the method of Zincke[3] with the slight modifications described in previous papers from this laboratory.[4]

The action of methyl alcohol on tetrabromorthoquinone gives rise to three compounds. Ten grams of tetrabromortho-

[1] Sodium amalgam also converted the α-benzyl alcohol body partially into the β-. We are unable to explain this reaction.

[2] This JOURNAL, **26**, 42 (1901).

[3] Ber. d. chem. Ges., **20**, 1777 (1887).

[4] This JOURNAL, **26**, 34 (1901); *Ibid.*, **30**, 522 (1903).

quinone were mixed with 10 to 15 cc. of methyl alcohol and allowed to stand at ordinary temperatures in a corked flask. After twenty-four hours the quinone had completely dissolved, and a red crystalline solid had been deposited in considerable quantity, which was filtered out and purified for analysis. The mother-liquors contained hydrobromic acid, as was shown by testing them with argentic nitrate, but the amount was so small, 0.3 gram from 10 grams of the tetrabromorthoquinone, that it was obviously due to some secondary reaction.

The second product was obtained by allowing the red compound to stand for a longer time in contact with its mother-liquor. After four or five days it began to change into a cream-colored, crystalline body, and after two weeks this change was almost complete. This same cream-colored substance was obtained by the action of fresh methyl alcohol on the red compound, or by allowing the mother-liquors from the red body to evaporate in an open vessel. It is not further changed by the action of methyl alcohol in the cold, even when continued for ten weeks.

The third product was obtained by boiling for a few minutes the cream-colored substance with methyl alcohol, or a mixture of equal parts of methyl alcohol and benzol, when, on cooling, it separated in pure white crystals.

Red Addition-compound of Tetrabromorthobenzoquinone and Methyl Alcohol.—This substance, the product of the brief action of methyl alcohol in the cold on tetrabromorthoquinone, was purified by recrystallization from hot benzol and ligroin (3 : 2), dried at 60° to 70°, and analyzed with the following results:

I. 0.2972 gram substance gave, on combustion, 0.1904 gram CO_2 and 0.0177 gram H_2O.

II. 0.2697 gram substance gave, by the Carius method, 0.4680 gram AgBr.

III. 0.2444 gram substance gave 0.4244 gram AgBr.

	Calculated for $(C_4Br_4O_2)_2CH_3OH$.	Found. I.	II.	III.
C	17.48	17.48	....	....
H	0.31	0.66	....	....
Br	73.65	....	73.83	73.90

These analyses, however, are not sufficient to establish the formula, as $(C_6Br_4O_2)_4CH_3OH$ contains the following percentages: C 17.36, H 0.23, Br 74.08, so that it is obvious that analyses cannot decide on the true formula. The experiments tried by us so far have not thrown any light on the nature of this substance, but we hope some work now in progress in this laboratory may lead to the desired result. The yield was good, as 10 grams of the tetrabromorthoquinone gave 8.5 grams of the red substance.

Properties of the Red Compound.—It crystallized from a hot mixture of benzol and ligroin in small, transparent, well-formed prisms of a cherry-red color. It melts sharply at 192° to 193°, apparently without decomposition, and seems to be entirely stable at all temperatures below its melting-point. It is soluble in alcohol or benzol. Hot dilute sodic hydrate converts it into a white, crystalline body, and the solution turns yellow. This color is discharged by the addition of an acid.

The α-Addition-compound of Methyl Alcohol and Tetrabromorthoquinone (*Tetrabromorthobenzoquinonemethylhemiacetal Oxide*), $(C_6Br_4O_2)_2CH_3OH$.—This substance is the cream-colored product of the prolonged action of methyl alcohol on tetrabromorthoquinone in the cold. It was purified by two crystallizations from warm benzol (boiling benzol might produce a partial decomposition), dried *in vacuo*, and analyzed with the following result:

0.1478 gram substance gave, by the Carius method, 0.2516 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2CH_3OH$.	Found.
Br	72.73	72.44

The result of this analysis is confirmed by our analytical work on the benzyl alcohol compound, which corresponds to this in every respect, so that there can be no doubt about the correct formula of the substance. Hydrobromic acid was found in the mother-liquors, if the substance was made by the action of methyl alcohol on tetrabromorthoquinone, but none

was detected when it was made by adding fresh methyl alcohol to the red substance just described.

Properties of the α-Addition-compound with Methyl Alcohol.—It crystallizes from warm benzol in short needles of a cream-white color. It is a substance of but slight stability as, although permanent in the cold, it begins to decompose slowly at temperatures as low as 50°, forming a red product. If dipped into a heated bath it melts at 178° to 182°, or rather decomposes to a brilliant red liquid, and this, like most other decomposition-points, is altered many degrees by changing the conditions of the heating. This decomposition is accompanied by an evolution of bromine, recognized by the color and smell of the vapor and its action with potassic iodide and starch. The red substance left behind showed the properties of the hexabrom-orthoquinopyrocatechin ether, $C_6Br_4O_2C_6Br_2O_2$, as it was insoluble in hot alcohol, did not melt below 300°, and crystallized from hot nitrobenzol in the flat, truncated needles characteristic of this body. The loss on heating was determined as follows:

0.1288 gram substance lost, on heating from 190° to 200° for twelve hours, 0.0261 gram.

	Calculated for $(C_6Br_4O_2)_2CH_3OH$.	Found.
Br_2+CH_3OH	21.82	20.26

This agrees with the results of the qualitative experiments and shows that the hexabromorthoquinopyrocatechin ether was formed with the loss of a molecule of bromine and one of methyl alcohol.

The substance is freely soluble in benzol or chloroform; slightly soluble in alcohol or ligroin. Hot strong hydrochloric acid decomposes it in a manner described in the section on the constitution of these bodies; dilute sodic hydrate dissolves it, and it is attacked by aniline in a hot benzol solution.

The β-Addition-compound of Methyl Alcohol and Tetrabrom-orthobenzoquinone, $(C_6Br_4O_2)_2CH_3OH$.—This substance was obtained by boiling the α-compound with methyl alcohol for a few minutes. The crystalline product was purified by one

crystallization from a mixture of equal parts of benzol and methyl alcohol, when it showed the constant melting-point 261°, and was dried at 100°, and analyzed with the following results:

I. 0.5152 gram substance gave, on combustion, 0.3377 gram CO_2 and 0.0254 gram H_2O.

II. 0.2569 gram substance gave 0.1713 gram CO_2 and 0.0157 gram H_2O.

III. 0.2158 gram substance gave, by the Carius method, 0.3697 gram AgBr.

IV. 0.1957 gram substance gave 0.3342 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2CH_2OH$.	Found. I.	II.	III.	IV.
C	17.73	17.87	18.18	....	....
H	0.46	0.55	0.68	....	....
Br	72.72	....	....	72.91	72.67

A molecular weight determination by the boiling-point method in benzol gave the following result:

0.6245 gram substance in 15 grams of benzol gave a depression $\Delta = 0°.123$.

	Calculated for $(C_6Br_4O_2)_2CH_2OH$.	Found.
Mol. wt.	880	883

Properties of the β-Methyl Alcohol Addition-compound.—It crystallizes from a mixture of benzol and methyl alcohol in white, rhombic plates, and melts at 261° apparently without decomposition. It is soluble in benzol or chloroform; less soluble in ethyl or methyl alcohol or ligroin. Strong hydrochloric acid has no effect on it even after long heating to 150° in a sealed tube, but chars it at 200°. Strong sulphuric acid dissolves it slowly, forming a colorless solution. On the other hand, long boiling with sulphuric acid of sp. gr. 1.38 produces no effect. Strong nitric acid does not act on it, but fuming nitric acid produces a greenish color. Sodic hydrate is without effect on it, and the same is true of boiling hydriodic acid of a strength of 50 per cent, and of aniline in boiling benzol solution. In fact we have not yet found any reagent that is likely to give decomposition-products which will throw light on its nature.

The most striking property of this substance is its great stability, since it is not decomposed by heat even at its melting-point, and resists the action of most reagents at high temperatures. In this respect it forms a marked contrast to the α-compound, which begins to decompose at 50°.

Monoacetate of the β-Methyl Alcohol Tetrabromorthobenzoquinone, $(C_6Br_4O_2)_2CH_3OCOCH_3$.—One and a half grams of the β-compound described above were mixed with 8 grams of acetic anhydride and 2 grams of fused sodic acetate, and the mixture heated in a flask with a return-condenser to about the boiling-point of the acetic anhydride (130° to 140°) for eight hours. A large quantity of warm water was then added and the whole shaken until all the acetic anhydride had been removed. The dark residue, which looked as if it had been charred, was filtered out, washed, and recrystallized from a mixture of benzol and methyl alcohol, in which most of the blackened material was insoluble, until it showed the constant melting-point 249°, when it was dried at 100° and analyzed with the following result :

I. 0.1350 gram substance gave, by the Carius method, 0.2224 gram AgBr.

II. 0.1795 gram substance gave 0.2926 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2CH_3OCOCH_3$.	Found. I.	II.
Br	69.42	70.12	69.37

Properties of the Acetate.—It crystallizes from a mixture of benzol and methyl alcohol in bunches of needles, which, when more developed, appear as prisms terminated by a single plane at an acute angle. It melts at 249° without apparent decomposition, and in solubilities resembles the mother-substance.

Action of Benzyl Alcohol on Tetrabromorthobenzoquinone.

Ten grams of tetrabromorthobenzoquinone were mixed thoroughly with 8 to 10 cc. of benzyl alcohol and allowed to stand at ordinary temperatures in a corked flask. After two hours the red color of the quinone had faded to pink, and after twenty-four hours the mixture had become a viscous, pinkish-white mass. This was treated with a cold mixture of ether

and ligroin (2 : 1) repeatedly, until the thick benzyl alcohol mother-liquor had been removed, leaving a granular white residue, which was purified for analysis by recrystallization from a hot mixture of ether and ligroin (5 : 1), or benzol and ligroin (3 : 1). The former solvent proved the more effective, although the latter gave better crystals. A mixture of chloroform and ligroin, although it seemed admirably adapted for this purification, should not be used, as the product from this crystallization gave, on analysis, percentages of bromine 1 or 2 per cent above the true value, possibly from imprisoned chloroform. As the melting-, or rather, decomposition-point of the substance is indefinite, this effect of the chloroform could be detected only by analysis. The substance was washed with ligroin and dried *in vacuo* for analysis. Of the following analyses, I. and II. were purified with ether and ligroin in the manner described, III. with benzol and ligroin, the solution being boiled for two hours, IV. with hot benzol and ligroin, while V. is a sample that was only washed with the mixture of ether and ligroin but not recrystallized.

I. 0.2502 gram substance gave, on combustion, 0.2160 gram CO_2 and 0.0240 gram H_2O.

II. 0.2517 gram substance gave, by the Carius method, 0.3954 gram AgBr.

III. 0.1546 gram substance gave 0.2430 gram AgBr.

IV. 0.2210 gram substance gave 0.3449 gram AgBr.

V. 0.1777 gram substance gave 0.2773 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2C_7H_7OH$	Found. I.	II.	III.	IV.	V.
C	23.85	23.56	....	....	....	....
H	0.84	1.07	....	....	....	....
Br	66.95	....	66.84	66.89	66.41	66.41

These analyses leave no doubt as to the composition of the substance, and the fact that it decomposes easily, when heated turning red, and at 165° to 170° melting to a red liquid, shows that it is closely related to the α-methyl compound described earlier. It is therefore the α-benzyl alcohol tetrabromorthobenzoquinone, or to name it according to Formula I., tetrabromorthobenzoquinonebenzylhemiacetal oxide.

Properties.—It crystallizes from a mixture of benzol and ligroin in colorless, flat prisms or broad needles. Its decomposition-point lies been 165° and 170°, when it is heated rapidly, where it melts to a brilliant red liquid. Even at temperatures as low as 120° a similar decomposition takes place slowly, shown by the appearance first of a pink and, finally, of a red color. Bromine is given off during this decomposition, which was recognized by its color, smell, and action on potassic iodide and starch paste. A quantitative experiment showed that this decomposition was exactly similar to that of the corresponding methyl compound.

0.2669 gram substance, when heated at 160° to 200° for five hours, lost 0.0772 gram.

	Calculated for $(C_6Br_4O_2)_2C_7H_7OH$.	Found.
$Br_2 + C_7H_7OH$	28.03	28.92

The substance therefore loses 1 molecule of bromine and one of benzyl alcohol. The residue was recognized as hexabromorthoquinopyrocatechin ether by its red color, its crystalline form, and its essential insolubility in all solvents except nitrobenzol.

The α-benzyl alcohol compound is soluble in benzol, ether, chloroform, glacial acetic acid, or boiling ethyl alcohol, giving colorless solutions; slightly soluble in ligroin. Strong hydrochloric or hydrobromic acid decomposes it at 100°. Sulphuric acid of sp. gr. 1.38 also acts on it when boiling. Fuming nitric acid turns it a deep bluish-green, and slowly dissolves it, forming a green solution which is decolorized by a drop of water. Hot dilute sodic hydrate decomposes it, and aniline in hot benzol converts it into the dianilinobromparaquinoneanil, melting at 173°. It has no immediate oxidizing effect on a mixture of potassic iodide and starch acidified with hydrochloric acid. Many of these reactions are described more in detail later in this paper.

The mother-liquors obtained in preparing this α-body from benzyl alcohol and tetrabromorthoquinone contained hydrobromic acid, probably due to a secondary reaction. On heating them to 100°, or warming with ethyl alcohol, a brilliant

red body was precipitated, which seemed to be the hexabromorthoquinopyrocatechin ether. As the α-body can be boiled with ethyl alcohol without reddening, these mother-liquors must contain some other substance. It was also observed that the crude α-substance obtained by washing out these mother-liquors dissolved completely in benzol or ethyl alcohol, showing that it contained none of the insoluble hexabromorthoquinopyrocatechin ether already formed.

β-Benzylalcoholtetrabromorthobenzoquinone, $(C_6Br_4O_2)_2C_7H_7OH$.—We did not succeed in preparing this substance by warming the α-body with benzyl alcohol according to the method which was so successful with the methyl compound, but we obtained it by treating the α-compound with acetic anhydride in the attempt to make an acetyl α-derivative. In carrying on this process the proper conditions must be observed carefully, as at high temperatures the β-compound is decomposed by acetic anhydride.

Two grams of the α-benzylalcoholtetrabromorthoquinone were mixed with 8 grams of acetic anhydride and 2 grams of fused sodic acetate, and the mixture heated at 60° to 70° until it became bright-red. It was then allowed to stand ten to fifteen minutes, when it was treated with an excess of cold water and the insoluble pink residue filtered out, dried at 40° to 50°, and purified by crystallization from a hot mixture of methyl alcohol and benzol, which left an undissolved residue of the hexabromorthoquinopyrocatechin ether, recognized by its red color and crystalline form. The crystallization of the soluble portion was continued until it showed the constant melting-point 216° to 217°, when it was dried at 100° and analyzed with the following results:

I. 0.1478 gram substance gave, by the Carius method, 0.2313 gram AgBr.

II. 0.1839 gram substance gave 0.2885 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2C_7H_7OH$.	Found. I.	II.
Br	66.95	66.60	66.77

The two analyses were made with different preparations. The stability of the substance shows that it belongs to the

same series as the α-methyl alcohol compound previously described.

Properties of the β-Benzylalcoholtetrabromorthoquinone.—It crystallizes in white, polygonal plates, which melt at 216° to 217° with no apparent decomposition. It is soluble in benzol or ether; slightly soluble in alcohol or ligroin. Neither dilute sodic hydrate nor aniline in hot benzol have any action on the substance, so that, like the β-methyl compound, it is remarkably stable, but it is not so stable as this substance, since it is decomposed by acetic anhydride, as described in in the following section. The formation of the β-compound by the action of sodium amalgam on the α-body is also described later.

Action of Acetic Anhydride on the β-Benzyl Alcohol Compound.

One gram of the β-compound was mixed with 6 grams of acetic anhydride and 1 gram of fused sodic acetate, and the mixture heated at 120° to 150° until all had dissolved, which usually took place in four to five hours. The dark-colored solution was then diluted with water and the gray crystalline precipitate recrystallized from a hot mixture of 3 parts of benzol with 1 part of methyl alcohol, until it showed the constant melting-point 208° to 209°, when the grayish-white crystals were washed with methyl alcohol, dried at 60° to 70°, and analyzed with the following result:

0.1190 gram substance gave, by the Carius method, 0.1547 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2C_7H_7OCOCH_3$.	Calculated for $C_6Br_4O_2C_7H_7OCOCH_3$.	Found.
Br	64.13	55.75	55.34

This analysis indicates that the acetic anhydride has decomposed the molecule of the β-compound, but it would be obviously unwise to discuss the nature of this decomposition on the present insufficient experimental data. This promising line of work will be continued in this laboratory during the coming year.

Reduction of the α-Benzylalcoholtetrabromorthoquinone.

Action of Zinc and Acetic Acid.—The α-benzylalcohol-

tetrabromorthoquinone was submitted to the action of coarsely powdered zinc and 95 per cent acetic acid in a series of test-tubes, 0.7 gram of the substance and about 10 cc. of acid being used in each tube. The action was started by warming for a few minutes, after which it was allowed to run by itself. The liquid turned very dark on cooling, and after standing for a short time deposited brownish needles, if the reduction had run well, which was not always the case by any means. These were filtered out and washed thoroughly with dilute acetic acid and warm water to remove the zinc acetate, after which they were purified by recrystallization from hot benzol. The substance was dried first in the air and afterward *in vacuo* for analysis.

0.1525 gram substance gave, by the Carius method, 0.2415 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2H_4C_7H_7OH$.	Found.
Br	66.67	67.40

The percentages of bromine in the reduced and original substances are so near together (66.67 and 66.95) that the analysis could not distinguish between them. The object of this analysis was to show that the reduction had not been accompanied by a decomposition of the molecule or the removal of bromine.[1]

Properties of the Reduction-product.—It crystallizes from benzol in clusters of pale straw-colored needles. It melts at 273° to 274°, and is decidedly more stable than the mother-substance. Its alcoholic solution gives a gelatinous precipitate with plumbic acetate; nitric acid oxidizes it to a bright-red substance, soluble in alcohol, and melting at 295° to 300°, the nature of which we did not have time to determine. It will be studied during the coming year. Dilute sodic hydrate converts it into a violet-colored substance, insoluble in water.

Action of Acetic Anhydride on the Reduction-product.

This work was undertaken to determine how many hy-

[1] Later work has shown that this substance has not the composition assigned to it above. The determination of its true formula must be left for further study.

C. L. J.

droxyl groups were contained in the reduced substance. The reduction-product melting at 273° to 274° was heated to 100° for a few minutes with acetic anhydride and a little dried sodic acetate; the solid dissolved at first, but later a white precipitate was thrown down. To make sure that the reaction was complete the mixture was allowed to stand several hours, and then treated with water, filtered out, thoroughly washed, and dried *in vacuo* for analysis.

0.1097 gram substance gave, by the Carius method, 0.1529 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2H_2(COCH_3)_2C_7H_7OCOCH_3$.	Found.
Br	58.93	59.29

The formula with two acetyl groups contains the following percentage of bromine:

$$(C_6Br_4O_2)_2H_2(COCH_3)C_7H_7OCOCH_3—Br\ 61.31.$$

There can be no doubt, therefore, that the reduction-product contains three hydroxyl groups.[1] The triacetate is a white substance melting at 275° to 280° and is decidedly stable for a body of this class.

Action of Sodium Amalgam.—Some of the α-benzylalcohol-tetrabromorthoquinone was suspended in water and exposed to the action of 3 per cent sodium amalgam in a flask filled with carbonic dioxide. After the action had been continued for five days the product was examined and found to melt at 170° to 180° to a red liquid. This decomposition-point is higher than that of the original α-body (165° to 170°), and, although little weight can be given to these decomposition-points, because they are so much influenced by the conditions of heating, we are inclined to think that in this case a new substance has been formed, as on recrystallizing the crude moist product from alcohol and ether the β-compound melting at 216° was obtained, and special experiments have shown that the α-compound is not converted into the β- by crystallization from a moist mixture of alcohol and ether, nor by

[1] Later work throws doubt on the correctness of this formula as well as on that of the reduction-product. C. L. J.

long standing with a strong solution of sodic carbonate. The study of this reaction must also be postponed till next year.

Behavior of Tetrabromorthobenzoquinone with Other Alcohols.

We have tried the action of the following alcohols on tetrabromorthobenzoquinone: Ethyl alcohol, normal propyl alcohol, isopropyl alcohol, isoamyl alcohol, allyl alcohol. In every case the action was allowed to run at ordinary temperatures, and products were obtained which were evidently mixtures of a white and a red substance. It seemed, therefore, that these higher alcohols acted in two ways, first by forming addition-compounds similar to that from methyl alcohol, and, secondly, by reducing some of the tetrabromorthoquinone to tetrabrompyrocatechin, which then acted on unaltered quinone to form the red hexabromorthoquinopyrocatechin ether. Under these circumstances we have postponed the study of the products from these other alcohols until the work on the simpler reactions with methyl or benzyl alcohol was more nearly finished.

Behavior of Tetrabromorthobenzoquinone with Toluol.

Five grams of the tetrabromorthoquinone were dissolved in 5 cc. of cold ordinary toluol (which had been redistilled but not dried over sodium), and the solution allowed to stand at ordinary temperatures in a corked flask. After several hours, or sometimes in a few minutes, if the mixture was shaken, the solution became pasty from the separation of a red addition-compound of tetrabromorthoquinone and toluol. If these red crystals were allowed to stand longer with their mother-liquor, after about eight days it was found that a paler red crystalline deposit had formed, which proved to be a compound of tetrabromorthoquinone and water. The mother-liquor from these crystals contained hydrobromic acid, and, if heated, or treated with alcohol or ether, formed a brilliant red, insoluble body, identified by its crystalline form as the hexabromorthoquinopyrocatechin ether. The crystals, on the other hand, contained none of this substance, as they were completely soluble in alcohol.

Tetrabromorthobenzoquinone with Toluol of Crystallization, $C_6Br_4O_2C_7H_8$.—The preparation of this substance has been described in the preceding section. It was obtained from the solution of tetrabromorthoquinone in toluol, even when it was saturated with water, as was shown by an experiment from which we expected to get more of the water compound by this device.

As it was very efflorescent, it was prepared for analysis simply by pressing as rapidly as possible between filter-paper.

0.9368 gram substance lost, when exposed to the air, 0.1745 gram. *In vacuo* there was an additional loss of 0.0019 gram.

	Calculated for $C_6Br_4O_2C_7H_8$.	Found. Air.	Vacuum.
Toluol	17.83	18.59	18.82

The numbers are as near as could be expected, considering the difficulties in the way of preparing the substance for analysis. Practically all the toluol (0.1742 gram) escaped after the substance had been exposed to the air for twenty-four hours. The residue was tetrabromorthoquinone. A second sample of the crystals, dried between filter-paper as before, was analyzed.

0.4300 gram substance gave, by the Carius method, 0.6247 gram AgBr.

	Calculated for $C_6Br_4O_2C_7H_8$.	Found.
Br	62.01	61.81

Properties of Tetrabromorthoquinone with Toluol of Crystallization.—It forms transparent, garnet-red prisms or large rectangular plates. It melts at 70° to 75°. As this is really a solution of the quinone in the separated toluol, no sharper result could be expected. Upon heating the melting-tube more intensely, the toluol vapors distil off and can be burnt at the mouth of the tube. If heated in an open tube to 100° for some time, the dark-red melted substance gradually becomes lighter, and at last solidifies to a yellowish-white, crystalline mass; the vapors given off contain bromine as shown by potassic iodide and starch and by bleaching litmus, and have the odor and action on the eyes of benzylbromide. The yellowish-

white residue, when recrystallized from a mixture of chloroform and ligroin, gives yellow, tapering needles, softening at 226° without reddening. When boiled with alcohol it gives a brilliant red substance. We were obliged to postpone the investigation of this product till the coming winter.

α-Compound of Tetrabromorthoquinone and Water.—The preparation of this substance by the action of common toluol on tetrabromorthoquinone has been described already. Ordinary benzol gave the same product. Analysis V. was made with a sample prepared with benzol. The preparation of this substance from apparently dry toluol or benzol shows that the tetrabromorthoquinone has a remarkably strong attraction for water; in fact, we did not succeed in getting our materials dry enough to avoid the formation of this water compound, but we prefer to postpone the description of our work in this direction until additional experiments have been tried.

The compound with water was purified by washing with a cold mixture of benzol and ligroin, which changed the color from light-red to yellowish-pink, and crystallizing from the same mixture hot. It was dried *in vacuo* and analyzed with the following results:

I. 0.2683 gram substance gave, on combustion, 0.1650 gram CO_2 and 0.0080 gram H_2O.

II. 0.2325 gram substance gave, by the Carius method, 0.4042 gram AgBr.

III. 0.2993 gram substance gave 0.5202 gram AgBr.

IV. 0.2565 gram substance gave 0.4447 gram AgBr.

V. 0.2709 gram substance gave 0.4724 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2.H_2O$.	Found.				
		I.	II.	III.	IV.	V.
C	16.63	16.78	....	....	....	....
H	0.23	0.34	....	....	....	....
Br	73.91	....	73.99	73.98	73.78	74.21

In purifying the substance a mixture of chloroform and ligroin must not be used, although it gives excellent crystals, as the analyses of such samples for halogens gave varying results too high for the theory. That this compound belongs

to the α-series is shown by the fact that it decomposes, giving a red compound when heated.

Properties of the α-Water Compound.—It crystallizes from benzol in colorless, tapering, flat needles. Its decomposition-point lies between 190° and 200°, when it is dipped into the heated bath, as between those temperatures it melts to a brilliant red liquid. This same decomposition takes place slowly at temperatures of about 160°, as shown by the appearance of the red color. Bromine was one of the products of this reaction, proved by its color, odor, bleaching power, and a test with potassic iodide and starch. The decomposition was studied quantitatively, as follows:

0.2080 gram substance lost, when heated for three hours at 190° to 200°, 0.0434 gram.

	Calculated for $(C_6Br_4O_2)_3.H_2O$.	Found.
$Br_2 + H_2O$	20.55	20.87

The residue was identified as the hexabromorthoquinopyrocatechin ether by its color, crystalline form, and other properties.

The substance is soluble in benzol, chloroform, alcohol, ether, or glacial acetic acid; very slightly soluble in ligroin. The three strong acids do not affect it in the cold, but hydrochloric acid (or hydrobromic acid) at 100°, and boiling sulphuric acid of sp. gr. 1.38, decompose it, as described in detail in a later section. Fuming nitric acid forms with it a pale greenish solution. Dilute sodic hydrate dissolves it easily, and the unaltered substance seems to be precipitated on acidification, but a strong solution of sodic hydrate does not dissolve it.

The β-Watertetrabromorthobenzoquinone, $(C_6Br_4O_2)_3.H_2O$.—This substance was made from the α-body by the regulated action of acetic anhydride in the way used for the preparation of the corresponding benzyl alcohol compound. Two grams of the α-substance were mixed with 8 grams of acetic anhydride and 2 grams of dried sodic acetate. The mixture turned bright-red almost immediately, and, after warming for a minute or two, was diluted with a large quantity of water

and the reddish precipitate filtered out. This was dried and treated with a mixture of 10 parts of methyl alcohol and one of benzol which dissolved most of it, but left a brilliant red residue. The solution, on evaporation, deposited a pure white, crystalline substance, which, after purification, showed the constant melting-point 221° to 222°. As it melts without decomposition, and crystallizes in polygonal plates like the other β-bodies, there can be little doubt that it is the β-watertetrabromorthoquinone. It is soluble in ether, benzol, or ligroin (difference from the α-body); slightly soluble in alcohol. Hot dilute sodic hydrate does not affect it, nor does aniline in a hot benzol solution.

The further action of acetic anhydride gave products with low melting-points, probably resulting from the splitting up of the molecule of the β-compound. Care must be taken, therefore, in preparing this substance that the action of the acetic anhydride does not run too far.

Certain Reactions of the Water and Alcohol Compounds.

This work was undertaken in the hope of settling the constitution of these substances and is described here, since it throws light on their properties, although it turned out of little value in the determination of their structure.

α-Compounds.

Action of Hydrochloric Acid.—One gram of the methyl alcohol compound, $(C_6Br_4O_2)_2CH_3OH$, heated with strong hydrochloric acid for thirty hours to 100° gave a deep-yellow liquid and long white needles. A drop of the acid liquor gave a deep-blue with potassic iodide and starch, and the vapors bleached moist litmus, showing the presence of chlorine or possibly bromine. On distilling with steam the first portions of the distillate were turbid, had a distinct chloroform odor, and gave the isonitrile test with aniline and sodic hydrate. The residue, after filtration, yielded on evaporation yellowish-white needles melting at 185° to 187°, giving a deep-green color with ferric chloride, and a precipitate with plumbic acetate in boiling aqueous solution. They are undoubtedly,

therefore, a pyrocatechin, and probably tetrabrompyrocatechin which melts according to Stenhouse at 187°, according to Zincke at 192° to 193°. The products identified were, therefore, chlorine (or bromine), chloroform, and a substituted pyrocatechin.

The benzyl alcohol compound, $(C_6Br_4O_2)_2C_7H_7OH$, gave with hydrochloric acid, under the same conditions, chlorine or bromine, either benzyl chloride or bromide, to judge by the smell, and a substituted pyrocatechin (proved by the usual reactions), which distilled with steam, and therefore was not tetrabrompyrocatechin, which cannot be distilled with steam. This was probably a chlorbrompyrocatechin, formed by the action of the chlorine on the tetrabrompyrocatechin, which must be the first product of the reaction. As this product seemed of but slight interest, it was not studied more thoroughly.

The water compound, treated with hydrochloric acid, gave bromine in considerable quantity.

Hydrobromic Acid.—When we studied the action of hydrochloric acid on the benzyl alcohol compound,

$$(C_6Br_4O_2)_2C_7H_7OH,$$

we found, as just stated, that the chlorine set free had a substituting action upon the tetrabrompyrocatechin. To remove this complication we took up the action with hydrobromic acid (redistilled, boiling-point 126°, containing 48 per cent of HBr). The substances were heated together in a sealed tube for thirty hours to 100° and the products were bromine, benzal bromide with perhaps benzyl bromide, and tetrabrompyrocatechin. The bromine was identified by its action with potassic iodide and starch paste. The benzal bromide was separated from the tetrabrompyrocatechin by distillation with steam, as the latter is not volatile under these conditions. The distillate contained 1 or 2 drops of oil with a strong odor like benzyl bromide. Upon heating about 5 cc. of the mixture of oil and water in a sealed tube to 125° for four hours the odor of benzaldehyde was very distinct, the irritating smell had vanished, and the aqueous liquid gave a test for

bromine with chlorine water. From this we infer that the oil was, in part at least, benzal bromide, but it is possible, in fact probable, that it also contained benzyl bromide, perhaps in considerable amount. The tetrabrompyrocatechin obtained as a residue from the distillation with steam was recognized by the melting-point 186° to 187° (Stenhouse found 187°, Zincke 192° to 193°), the dark green color with ferric chloride, the precipitate with plumbic acetate, and the formation of the red tetrabromorthoquinone with nitric acid. It seemed evident from these results that the acid breaks up the α-benzyl alcohol compound into tetrabromquinone and benzyl bromide. The quinone then sets free bromine from the hydrobromic acid, becoming itself tetrabrompyrocatechin, and the bromine converts the benzyl bromide wholly or in part into benzal bromide.

Action of Sulphuric Acid.—The α-benzyl alcohol compound, $(C_6Br_4O_2)_2C_7H_7OH$, was boiled in a flask with a return-condenser for three hours with sulphuric acid of sp. gr. 1.38. Oily drops were observed in the condenser, and there was a strong, irritating odor. The principal product, a yellowish-red solid, on treatment with alcohol, left a considerable amount of the red hexabromorthoquinopyrocatechin ether recognized by the usual properties and the following analysis :

0.2149 gram substance gave, by the Carius method, 0.3494 gram AgBr.

	Calculated for $C_4Br_4O_2C_6Br_2O_2$.	Found.
Br	69.77	69.19

Tetrabrompyrocatechin gave none of the ether on similar treatment with sulphuric acid. The filtrate from the ether contained bromine and hydrobromic acid, but this observation has not much significance, as it was found that the red ether, when boiled with a few drops of bromine and sulphuric acid, gave hydrobromic acid, and that tetrabromorthoquinone also formed hydrobromic acid when boiled with water for two hours.

The water compound, $(C_6Br_4O_2)_2.H_2O$, treated in the same way with sulphuric acid of sp. gr. 1.38, gave the red hexabromorthoquinopyrocatechin ether.

β-Compounds.

The methyl alcohol compound, $(C_6Br_4O_2)_2CH_3OH$, melting at 261°, was the only one studied. Hydrochloric acid had no action on it even at 140° to 160° for thirty hours, as was proved by recovering the amount of compound used entirely unaltered. After heating to 200° for forty-eight hours the substance was charred.

Hydriodic Acid.—The β-methyl alcohol compound was boiled with hydriodic acid (50 per cent HI) for forty minutes in a flask with a return-condenser, but there was no action, as we recovered the whole of the substance unaltered.

Sulphuric acid, of sp. gr. 1.38, also had no action on the β-methyl alcohol compound after boiling for two hours. It is evident from these experiments that the β-methyl alcohol compound is a remarkably stable substance. Similar experiments with the β-benzyl alcohol compound will be tried in this laboratory, as it seems to be less stable than the methyl alcohol body.

Addition-compounds of Acetic Acid and Tetrabromorthobenzoquinone.

In the first paper of this series, W. Koch and one of us[1] described a white compound formed by the action of glacial acetic acid on tetrabromorthoquinone, but owing to its remarkable stability no formula could be assigned to it with certainty. We have made little progress on the continuation of this work, because we thought it wiser to study the more manageable alcohol compounds first, in order to gain experience which would help us to solve this difficult problem. All the work described in this section, therefore, must be considered preliminary experiments.

In preparing the substance by the method given in the paper already referred to we obtained by the repeated evaporation of glacial acetic acid in contact with tetrabromorthobenzoquinone on the steam-bath a yellowish-white residue, which, on treatment with hot alcohol, deposited a slight amount of a vermilion-red precipitate. This increased in

[1] This JOURNAL, **26**, 42 (1901).

quantity as the boiling with alcohol was continued, so that after fifteen to twenty minutes boiling the red insoluble substance seemed to form the only product of the reaction. The red product was identified by its properties as hexabromorthoquinopyrocatechin ether. It was also formed when the crude product was boiled with acetone, ethyl acetate, or water. That none of it existed in the crude product of the action of acetic acid on orthoquinone was shown by the fact that this dissolved completely in cold benzol. We must therefore correct the statement of Koch and one of us that the red insoluble compound was formed by the action of acetic acid on tetrabromorthoquinone. The small amount observed by them was formed by the subsequent treatment of the crude product with alcohol.

To obtain the white compound, the crude product was extracted as quickly as possible with hot alcohol, the extract allowed to stand for a time, filtered, and precipitated with water. This precipitate was warmed for some time with a little glacial acetic acid and then dissolved in boiling glacial acetic acid, filtered from the red insoluble portion, and crystallized from the boiling acid. It was dried by exposure to dry air at 40° to 50° and analyzed with the following result:

0.1761 gram substance gave, by the Carius method, 0.2865 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2CH_3OH$.	Found.
Br	70.48	69.26

These results leave much to be desired, but can hardly be brought into harmony with any other probable formula.

Properties.—It crystallizes from glacial acetic acid in large, yellowish-white, efflorescent, rectangular plates or prisms. It melts at 220° to 230° with decomposition, forming a red liquid. On being heated for several hours near its melting-point it gave up bromine, detected by its odor and the reaction with potassic iodide and starch, and left a brilliant red substance, which, however, did not seem to be the hexabromorthoquinopyrocatechin ether to judge by the form of its crystals. The loss in weight, too, did not agree with that calculated for

$CH_3COOH + Br_2$. The acetic acid compound is soluble in alcohol, benzol, ether, chloroform, or glacial acetic acid; very slightly soluble in ligroin. Dilute sodic hydrate dissolves it easily with a dark color, indicating a decomposition of the substance. Aniline in hot benzol converts it into the dianilinobromparaquinone anil. All these properties show that the substance is not identical with the very stable white compound prepared by Koch and one of us.[1] That a compound such as this was formed at first is indicated in the paper referred to by the statement that the crude product was freely soluble in alcohol, but, as the crystallization from glacial acetic acid continued it became less and less so, until, when pure, it was nearly insoluble in alcohol. To judge from these preliminary experiments, the substance prepared by us corresponds to the α-addition-compounds of alcohols and tetrabromorthoquinone, and it seems probable that the more stable body is in some way related to the β-compounds.

Glacial acetic acid, if allowed to stand in the cold with tetrabromorthoquinone, gave two products, which seemed to be entirely different from any of those as yet studied by us. This work will be continued.

Action of Acetophenone on Tetrabromorthobenzoquinone.

This work was taken up in the hope that it would throw light on the action of acetic acid on the tetrabromorthoquinone. At first the action was carried on hot, as it was in this way that the acetic acid compound had been obtained. Later, after the work with alcohols, the action was carried on at ordinary temperatures with a different result.

Action at the Boiling-point.—Two grams of tetrabromorthoquinone were boiled in a flask with a return-condenser with 25 cc. of acetophenone. On standing over night the very dark-colored product deposited pale-yellow, long needles, which, after purification by washing with acetic acid and crystallization from a mixture of alcohol and chloroform, were recognized as triphenylbenzol by the melting-point, 171°, and the following analysis:

[1] This JOURNAL, **26**, 42 (1901).

0.1392 gram substance gave, on combustion, 0.4773 gram CO_2 and 0.0725 gram H_2O.

	Calculated for $C_6H_3(C_6H_5)_3$.	Found.
C	94.12	93.53
H	5.88	5.78

It is evident that the tetrabromorthoquinone was decomposed under these circumstances with the formation of hydrobromic acid (detected in the crude product), which then converted the acetophenone into the symmetrical triphenylbenzol. All attempts to isolate the other products of the reaction failed. Nor were we more successful when the reaction was carried on at as low a temperature as 65°.

Action at Ordinary Temperatures. Tetrabromorthobenzoquinone with Acetophenone of Crystallization.—Five grams of the tetrabromorthoquinone were dissolved in 5 cc. of cold acetophenone, and the clear solution allowed to stand twenty-four hours, when it was found that well-formed, transparent, red prisms had been deposited. As they effloresced rapidly, they were prepared for analysis by pressing them quickly in filter-paper.

0.7064 gram substance lost, *in vacuo* in twenty days, 0.1567 gram, which increased by 0.0060 gram after twelve days more.

	Calculated for $C_6Br_4O_2C_6H_5COCH_3$.	Found.	
		20 days.	32 days.
$C_6H_5COCH_3$	22.06	22.19	23.04

The residue was tetrabromorthoquinone.

0.3103 gram substance gave, by the Carius method, 0.4234 gram AgBr.

	Calculated for $C_6Br_4O_2C_6H_5COCH_3$.	Found.
Br	58.82	58.03

These results are as good as could be expected, when the imperfect method of drying the substance is remembered.

It forms red prisms, which melt, or rather dissolve in the liberated acetophenone between 50° and 60°. In its solubilities it resembles tetrabromorthoquinone. On long standing with acetophenone it is converted into a yellow crystalline

substance, which resembles the α-addition-compounds in properties, but its analysis gave such perplexing results that we think it wiser to say no more about it until further experiment has made its nature clear.

The action of other reagents on tetrabromorthoquinone was also studied, but in view of the strong attraction it shows for water we prefer to postpone all account of these experiments until they have been repeated under more carefully regulated conditions. It is worth mention, however, that ligroin (boiling from 40° to 70°) gave with the tetrabromorthoquinone yellowish-red prisms, which were white when powdered. This is probably the white product obtained by Zincke[1] from the action of a mixture of ether and ligroin on tetrabromorthoquinone.

Certain Reactions of Tetrabromorthobenzoquinone.

These observations were made usually as parallel experiments in the course of our work on the addition-compounds, and may be collected here for convenience.

Decomposition by Heat.—About 1 gram of tetrabromorthoquinone was heated in an air-bath at 130° to 150°. Bromine was evolved, as shown by the odor and test with potassic iodide and starch. The residue, which was somewhat lighter red than the quinone, upon extraction with boiling alcohol was separated into a white soluble substance melting between 180° and 190°, and giving no test for a pyrocatechin with ferric chloride, and a red substance insoluble in the alcohol, which looked like hexabromorthoquinopyrocatechin ether. Upon crystallizing this body from nitrobenzol rather indefinite crystals were obtained instead of the flat truncated needles characteristic of the ether, and an analysis gave 68.48 per cent of bromine instead of 69.77. It is safe to assume that the presence of the impurity indicated by this analysis caused the difference in the crystalline form, and that the substance is really the pyrocatechin ether.

Decomposition by Boiling Water.—Two grams of the tetrabromorthoquinone were mixed with 50 cc. of water by thor-

[1] Ber. d. chem. Ges., **20**, 1778 (1887).

ough shaking, and then boiled for an hour in a flask with a return-condenser. The liquid faded from red to a pale straw-color, and, when filtered and evaporated, deposited a yellowish compound, giving only a faint test for a pyrocatechin with ferric chloride. It also contained hydrobromic acid. The insoluble residue, after extraction with boiling alcohol, consisted of hexabromorthoquinopyrocatechin ether.

Fuming nitric acid dissolved tetrabromorthoquinone to a clear purple-red, or claret-colored solution. Dilution with water precipitated the quinone unaltered. On heating the quinone with fuming nitric acid a pale yellowish solution was formed.

The study of these addition-compounds of tetrabromorthobenzoquinone will be continued in this laboratory, and its action with other reagents investigated. The attempt will be made also to prepare similar addition-compounds from other orthoquinones.

CAMBRIDGE, MASS., Aug. 22, 1903.

ACTION OF ALCOHOLS ON THE TETRAZONIUM CHLORIDES DERIVED FROM BENZIDINE AND FROM ORTHOTOLIDINE.[1]

BY J. H. C. WINSTON.

The investigation, the results of which are presented in this article, is a continuation of the larger investigation[2] on the action of alcohols on diazo compounds that has been carried on for a number of years past in this laboratory under the guidance of Professor Remsen. It deals especially with the action of methyl, ethyl, and propyl alcohols under different conditions on the tetrazonium chlorides obtained from benzidine hydrochloride and from orthotolidine hydrochloride.

Preparation of Metaditolyltetrazonium Chloride.—The tolidine used was prepared from commercial *o*-tolidine. This

[1] From the author's dissertation submitted, June, 1899, to the Board of University Studies of the Johns Hopkins University, in conformity with the requirements for the degree of Doctor of Philosophy. The investigation was undertaken at the suggestion of Professor Remsen and carried on under his guidance.

[2] For earlier investigations in this series see This JOURNAL, **4**, 374; **8**, 243; **9**, 387; **11**, 319; **15**, 124, 301, 320, 379; **16**, 235; **19**, 163, 563, 831; **20**, 229, 298, 458.

was purified by converting it into the hydrochloride, treating this in solution with bone-black, and precipitating the tolidine with potassium hydroxide. It crystallizes from water in beautiful pearly leaves, melting at 126°.5. In the preparation of the tetrazonium chloride it was found best to use freshly-made tolidine hydrochloride, precipitated in finely divided condition by addition of strong hydrochloric acid to a water solution of the hydrochloride. To prepare the tetrazonium chloride, take tolidine hydrochloride and water in the proportion of 3 parts of water to 1 of the salt. Add a part of the salt first and then pass nitrous fumes from arsenious oxide and nitric acid into the paste. As this clears up, add more of the salt, and continue this until the action is complete and a clear, light straw-yellow solution is obtained. Pour this into about three times its volume of 95 per cent alcohol, which has been previously cooled in a freezing-mixture of salt and ice. The tetrazonium salt is at once precipitated in the form of a flocculent yellow substance. This is then filtered off through a Büchner funnel, washed with alcohol and ether, and spread on drying-paper. The yield is about 80 per cent of the theoretical.

Action of Absolute Methyl Alcohol upon Metaditolyltetrazonium Chloride.—The action was carried on in a flask connected with a return-condenser, the flask being placed on a water-bath. The decomposition began only when the temperature reached almost that of the boiling-point of the alcohol, and then proceeded smoothly with the copious evolution of nitrogen until the reaction was completed and a perfect solution resulted. This required half an hour. The solution was then boiled for a few moments to insure complete decomposition. During the whole operation no odor of aldehyde was perceptible. As the decomposition proceeded the alcoholic solution changed color, gradually darkening, until at the end it was of a deep red color. On allowing the solution to cool, crystals in the form of reddish leaves separated, which were removed by filtration. Upon evaporation of a large part of the alcoholic mother-liquor a very small crop of crystals was obtained. The rest of the alcohol was then removed by distillation and was of a

slightly yellow color. This was poured into a beaker and 6 volumes of a saturated solution of sodium chloride added, but no oil separated. The color of the alcohol was probably due to particles of the tarry residue, mechanically carried over during the process of distillation. The tarry oil remaining in the distillation-flask was easily soluble in ordinary alcohol, but from this solution nothing of value was ever obtained. Purification was attempted by means of animal charcoal, but the reddish color could not be thereby removed. On partial evaporation nothing was obtained in crystalline form, and on complete evaporation of the alcohol the same unpromising oil resulted. Some of this was allowed to stand for weeks, in the hope that something would crystallize out. Solidification by means of a freezing-mixture was attempted, but it remained always the same tarry oil. Some of it was put in a distillation-flask and subjected to distillation. The residue remaining in the flask after the last traces of alcohol and water were removed solidified to a non-crystalline black cake, from which nothing definite could be obtained. It was thought that if any of the hydrocarbon corresponding to this tolidine, which is known to be an oil, was present it could be separated from the tar by distillation with water vapor, so to the flask containing the tar a little water was added, and then steam passed through the flask, but no oil was carried over with the water vapor. The crystals, which had been obtained by the action of methyl alcohol on tetrazo-*m*-ditolyl chloride, were dissolved in ordinary alcohol, the solution decolorized with animal charcoal, and from this, on allowing a hot concentrated solution to cool, the substance was obtained in the form of beautiful, almost colorless, leaves. These were recrystallized until the melting-point became constant, and were then obtained as silvery leaves having the sharp melting-point 145°.5. This substance is insoluble in water, very sparingly soluble in cold alcohol and ether, rather soluble in boiling alcohol. The difference in solubility in alcohol at its boiling temperature and a few degrees below, is very marked.

Two analyses gave the following results:

I. 0.2000 gram substance gave 0.5801 gram CO_2 and 0.1337 gram H_2O.

II. 0.2000 gram substance gave 0.5812 gram CO_2 and 0.1336 gram H_2O.

The calculated percentages of the elements for dimethoxy-*m*-ditolyl ($C_{14}H_{12}(OCH_3)_2$) are :

	Calculated.	Found. I.	Found. II.
C	79.34	79.10	79.11
H	7.44	7.43	7.43
O	13.22	13.47	13.46

There are two ways in which the reaction between tetrazonium chloride and methyl alcohol might take place. The two reactions are represented in the following equations :

I. $C_{14}H_{12}N_4Cl_2 + 2CH_3OH = C_{14}H_{14} + 2CH_2O + 2N_2 + 2HCl$;

II. $C_{14}H_{12}N_4Cl_2 + 2CH_3OH = C_{14}H_{12}(OCH_3)_2 + 2N_2 + 2HCl$.

It is observed that in the case of the substances brought together in the decomposition described above and under the conditions indicated, the reaction takes place in accordance with the second equation, and, indeed, the most careful search failed to reveal any evidence that the first reaction takes place at all when this tetrazonium salt is treated with methyl alcohol under the given conditions. It was considered advisable to vary the conditions of the reaction to determine how the decomposition is best effected, and also to study the effects of variations in temperature and dilution of the alcohol, as well as the presence of certain substances known to affect the reaction, generally speaking.

Decomposition of the Tetrazonium Salt at Room Temperature.—About 15 grams of the diazo compound were placed in a half-liter flask and 250 cc. of absolute methyl alcohol added, and the mixture allowed to stand at room temperature for a fortnight, alcohol being added from time to time to make up for evaporation. By the end of this time most of the salt had gone into solution and the alcohol had turned dark-red, but at no time was an evolution of nitrogen noticeable, neither was the odor of aldehyde perceptible. The flask was now attached to a return-condenser and the alcohol boiled on a water-

bath, when nitrogen was evolved freely and the reaction was complete in half an hour. The yield of the crude ether was a little over 4 grams, but this was not as pure as that made in the decomposition of the freshly-prepared salt. All efforts to obtain the hydrocarbon from the alcohol distilled off and from the residue in the distillation-flasks were as futile as those described above.

Decomposition of the Tetrazonium Salt at the Boiling Temperature of Methyl Alcohol.—Fifteen grams of the same tetrazonium salt were decomposed with absolute methyl alcohol at the boiling temperature of the alcohol. The decomposition was complete in half an hour, the evolution of nitrogen being rapid and the solution reddening as before. About 4 grams of the ether were obtained, which substance was not as deeply colored as that obtained in the preceding experiment. As before, no other product was isolated, and it seems that only the "methoxy" reaction takes place in this decomposition. An attempt was next made to determine the effect of diluting the alcohol with water.

Decomposition of the Tetrazonium Salt with Dilute Methyl Alcohol.—Twenty-three grams of the salt were decomposed with methyl alcohol diluted with 5 per cent of its volume of water. The decomposition was accomplished in the usual manner by heating the mixture to the boiling-point of the alcohol, when the reaction proceeded smoothly and quickly. On cooling, 5 grams of dimethoxy-*m*-ditolyl separated in crystalline form. The reaction was not as clean as in the cases in which the absolute alcohol was used, the solution becoming more deeply colored and the product more impure.

Eighteen grams of the salt were treated with methyl alcohol diluted with 10 per cent of its volume of water and the decomposition effected as before. The results were in every way similar. The yield was 4.5 grams of the ether.

After this, many other similar experiments were carried on. The water solution of the salt, after the diazotization was completed, was added to ten times its volume of methyl alcohol and the salt decomposed in the usual manner. The per-

centage of the ether obtained was in every case nearly the same. When, however, the alcohol contained as much as 40 or 50 per cent of water, the yield of the ether was materially diminished and the formation of tarry products relatively greater. In all cases of dilution the product was not as pure as when the absolute alcohol was used, so that, although the yield of the ether was not materially better when the absolute alcohol was employed, than in those cases when the alcohol was diluted to within 20 per cent of its volume with water, yet the absolute alcohol method proved to be the best, as the excess of alcohol was ready for another decomposition as soon as distilled off, and the reaction by this method was cleaner in every way. I decomposed in this way 180 grams of the tetrazonium salt and obtained a yield of 42 grams of the crude ether, which, when purified, gave 33 grams of pure dimethoxy-*m*-ditolyl.

Decomposition of the Tetrazonium Chloride with Ethyl Alcohol.—The decomposition was carried on at the boiling temperature of the alcohol. Throughout the operation aldehyde was given off. On allowing the alcoholic solution to cool, crystals were obtained which resembled those obtained by the decomposition with methyl alcohol. From 20 grams of the salt 2.25 grams of the crude product were obtained. The alcohol was then distilled off and six times its volume of a saturated solution of sodium chloride added, but nothing was obtained in this way. The tarry oil in the distillation-flask was then subjected to distillation with steam, and a few drops of a yellow oil were obtained. These experiments were repeated many times, and the yields were relatively the same in every case. The amount of the oil formed was never determined accurately, but it appeared to be produced in nearly the same amount as the crystalline solid. It is very difficultly volatile with water vapor. Its density is about the same as that of water. After a sufficient quantity of it had been obtained, it was taken up from the water with ether, dried with calcium chloride, and subjected to distillation. It passed over almost wholly at 280° to 281°, and was recognized as *m*-ditolyl, which has a specific gravity of 0.9993 at 16°. This

substance was discovered by Schultz,[1] in 1884, as one of the products of the action of nitrous acid on an alcoholic solution of *o*-tolidine. He described it as a yellow oil boiling at 281°, which, by oxidation with potassium bichromate and sulphuric acid, yields isophthalic acid. By careful oxidation in acetic acid solution with the calculated amount of chromic acid he obtained a new acid, diphenyldi-*m*-carboxylic acid, melting at 193°. In 1888 Stalle[2] repeated the experiments of Schultz, and made many derivatives of this hydrocarbon. He found 289° to be its boiling-point. A little later Perrier[3] succeeded in oxidizing one of the methyl groups by means of nitric acid (sp. gr. 1.14), and thus obtained the monocarboxylic acid.

The crystalline solid, which had been obtained in the decomposition described above, was dissolved in alcohol and decolorized with animal charcoal. It is not as soluble in alcohol as is the product obtained from the reaction of methyl alcohol with the diazo compound, and the difference in solubility at the boiling temperature and a few degrees below is even more marked than is this difference in the case of dimethoxy-*m*-ditolyl. It is insoluble in water, practically insoluble in cold alcohol and ether. When the alcoholic solution is allowed to cool it crystallizes therefrom in beautiful pearly plates, melting sharply at 154°. This compound was therefore supposed to be diethoxy-*m*-ditolyl, first obtained by Schultz by the action of nitrous acid on an alcoholic solution of *o*-tolidine. He gives its melting-point as 156°. About two years later the same substance was made by Hobbs,[4] by treating the potassium salt of dihydroxy-*m*-ditolyl with ethyl iodide.

I. 0.2000 gram substance gave 0.5885 gram CO_2 and 0.1450 gram H_2O.

II. 0.2000 gram substance gave 0.5916 gram CO_2 and 0.1451 gram H_2O.

III. 0.2000 gram substance gave 0.5886 gram CO_2 and 0.1444 gram H_2O.

[1] Ber. d. chem. Ges., **17**, 468.
[2] *Ibid.*, **21**, 1096.
[3] Compt. rend., **114**, 484.
[4] Ber. d. chem. Ges., **21**, 749.

	Calculated.	Found. I.	II.	III.
C	80.0	80.25	80.70	80.30
H	8.1	8.05	8.10	8.00
O	11.9	....	....	....

Thus it is seen that when the tetrazonium chloride is decomposed with methyl alcohol the "alkoxy" reaction only takes place, while, when the decomposition is effected with ethyl alcohol, both the "hydrogen" and the "alkoxy" reactions take place. The latter decomposition is not as clean as the former, and the definite products are not formed in as large quantity.

Decomposition of the Tetrazonium Salt with Ethyl Alcohol under Varying Conditions of Temperature and Dilution of the Alcohol.—Some of the salt was allowed to stand in contact with absolute ethyl alcohol for two weeks. The odor of aldehyde was noticeable at any time if the mixture was shaken up, but at the end of this time the greater part of the salt was still undecomposed. The flask containing the partially decomposed salt was attached to a return-condenser and the alcohol heated to boiling, when the nitrogen was evolved and the decomposition completed. The diethoxy-*m*-ditolyl and *m*-ditolyl were separated as before and their relative amounts were the same as previously found.

The decomposition was next effected with ordinary 95 per cent alcohol by the usual method of heating the alcohol to boiling. The yields were the same.

Many experiments were carried on with various dilutions, as the result of which it was found that the relative amounts of the oil and crystalline solid were not materially affected by diluting the alcohol with water up to 20 per cent of its volume, and also that the total yields were about the same. The reaction in these cases seemed very nearly as clean as when the absolute alcohol was used. When the alcohol was diluted with more than 20 per cent of its volume of water the yields diminished, and with increasing dilution the reaction was less clean and the amount of tar formed greater. Most of the diethoxy-*m*-ditolyl used in this investigation was obtained as a

by-product in the preparation of dimethoxy-*m*-ditolyl. The alcohol-water mixture, from which most of the tetrazonium chloride had been precipitated, was poured into a flask and the salt therein remaining decomposed by heating the solution on a water-bath. Half of the alcohol was then distilled off and the solution allowed to cool, when the diethoxy-*m*-ditolyl crystallized out. No effort was made to separate the *m*-ditolyl because another method of making this compound was discovered by which it could be obtained in any desired amount and in almost quantitative yield. Our attention was next turned to the action of nitric acid on the two phenol ethers which had been made.

Action of Nitric Acid on Dimethoxy-m-ditolyl and on Diethoxy-m-ditolyl.—Ordinary concentrated nitric acid converts dimethoxy-*m*-ditolyl into a tetranitro product that crystallizes in needles and melts at 130°.5. Estimations of nitrogen gave 13.5, 13.24, and 13.4 per cent. The calculated percentage for a tetranitro product is 13.27.

Fuming nitric acid gave the best results in the case of diethoxy-*m*-ditolyl. The product crystallizes in rhombs or needles resembling dinitrobenzene. It melts at 142°. Nitrogen found 12.9, 12.5, and 12.6 per cent. Calculated 12.44 per cent.

Preparation of Dihydroxy-m-ditolyl, or o-Dicresol.—In 1888 Gerber[1] and Hobbs[2] prepared this substance by boiling a water solution of metaditolyltetrazonium chloride, and obtained it in the form of large, broad needles, melting at 157°. It was found that unless the solution was very dilute, very little of the *o*-dicresol was formed and that a few drops of sulphuric acid increased the yield. I will describe one experiment, in which the proportions were such as to give the best results. Ten grams of tolidine hydrochloride were diazotized in the usual manner. The water solution of the diazo compound was poured into a 3-liter flask and 1500 cc. of water were added. After the addition of a few drops of sulphuric acid the whole was boiled for fifteen minutes. On cooling,

[1] Ber. d. chem. Ges., **21**, 749.
[2] *Ibid.*, **21**, 1665.

the tar formed became attached to the sides of the flask, and from the clear solution the *o*-dicresol was obtained in the form of large, broad needles. The yield was 2.5 grams. The crystals were further purified by recrystallization from boiling water and melted sharply at 155°. *o*-Dicresol is very soluble in alcohol and remains in solution as long as any alcohol is present, but when the alcohol has all evaporated the substance is obtained in the form of plates, always of a brownish color. A water-alcohol mixture was found to be an excellent solvent for *o*-dicresol, from which it crystallizes in needles perfectly white.

This substance was also prepared by the method of Graebe by the action of halogen acids on phenol ethers in sealed tubes at high temperatures.

Action of Sodium Methylate on the Tetrazonium Compound.—Twenty grams of the tetrazonium chloride were decomposed by a solution of sodium methylate in methyl alcohol. The sodium methylate was made by dissolving 15 grams of clean, bright, metallic sodium in 250 cc. of absolute methyl alcohol, the alcohol being kept in ice-water while the reaction was taking place. This solution was used for the decomposition of the tetrazonium compound, being kept in ice-water all the while. The tetrazonium compound was added in small portions from time to time and the mixture well shaken. The action took place energetically, nitrogen being freely evolved. For the decomposition of 20 grams of tetrazo compound about fifteen minutes were required, the temperature being kept below 20°. The solution turned red at first, and finally almost black, and much matter of a tarry nature separated. After the decomposition was complete the methyl alcohol was distilled off and the contents of the flask subjected to steam-distillation. Drops of an oil were thus carried over. This was taken up in ether, dried, and distilled. It was easily recognized as *m*-ditolyl. This oil is not very volatile with steam and it is almost impossible to separate all of it from the tar by this means. The yield of the crude *m*-ditolyl was 5 grams.

Action of Methyl Alcohol on the Tetrazonium Compound in

the Presence of Sodium Hydroxide.—Twenty grams of the tetrazonium chloride were decomposed with 200 cc. of absolute methyl alcohol, in which 10 grams of sodium hydroxide had been dissolved. As before, the alcohol was cooled with ice and the tetrazonium compound added in small portions. The reaction proceeded exactly as in the preceding experiment, being very energetic, almost violent at first. As soon as the reaction was complete the alcohol was distilled off, and the residue distilled in steam. *m*-Ditolyl passed over with the steam, which was separated from the water with ether. Five and a half grams were thus obtained. In both of these experiments, as was to be expected from earlier work in this laboratory, the "hydrogen" reaction took place. A careful search was made for any ether that might have been formed at the same time, but the search was fruitless.

Action of Methyl Alcohol on the Tetrazonium Compound in the Presence of Zinc Dust.—Ten grams of the tetrazonium compound were placed in a flask containing 10 grams of zinc powder and 100 cc. of absolute methyl alcohol. There was no immediate action, though the solution darkened gradually, and on shaking a slight evolution of nitrogen was observed, but the decomposition was very slow. After standing for twenty-four hours most of the tetrazonium compound remained undecomposed. The flask containing the mixture was then attached to a return-condenser and heated upon a water-bath. The decomposition proceeded smoothly and the reaction was soon over, the alcohol being of a light-yellow color. This was filtered to remove the zinc dust and then the methyl alcohol distilled off. There remained in the distillation-flask a dark-red oil, which was distilled in steam and separated from the water with ether. The yield from 10 grams of the tetrazonium compound was 4.5 grams of crude *m*-ditolyl. In this decomposition there was no formation of anything of a tarry nature and the reaction was perfectly clean. In this, as in the decompositions in the presence of sodium hydroxide and sodium methylate, a strong odor resembling aldehyde was noticed, which was probably paraldehyde. When 10 grams of the tetrazonium compound were

decomposed with ethyl alcohol in the presence of zinc dust the decomposition took place in exactly the same manner. At the end of the operation the solution cleared up to a straw color, as before. The yield of *m*-ditolyl from 10 grams of the tetrazonium compound was 4 grams. It was thought advisable to make quite a quantity of *m*-ditolyl and repeat, to some extent, the experiments of Schultz.

One hundred grams of tolidine hydrochloride were diazotized, and the tetrazonium salt precipitated, filtered, washed, and dried in the usual manner. It was then decomposed with methyl alcohol in the presence of zinc dust. The clear, yellow solution thus obtained was filtered from the zinc and the alcohol distilled off. A considerable amount of the reddish oil remained in the flask. To the water-alcohol mixture from which the tetrazonium compound had been precipitated and which was already of a reddish color, zinc dust was added, the flask attached to a reflux-condenser, and the mixture boiled. The decomposition of the tetrazonium compound therein remaining was thus effected, and the solution cleared up to a light-yellow color. The zinc dust was filtered off and most of the alcohol removed by distillation, when an oil separated. This was removed by means of a separating-funnel and added to that obtained from the decomposition with absolute methyl alcohol and zinc dust. The oil was then taken up in ether, dried with calcium chloride, and distilled from a flask of appropriate size. Forty-eight grams of *m*-ditolyl, boiling at 278° to 281°, were thus obtained. The yield of the pure substance is thus 76 per cent of the theoretical amount. The real yield was even greater than this, the operation being attended with considerable loss. After all of the *m*-ditolyl had distilled off, the thermometer rose rapidly to 360°, above which point a few drops of an oil of a strong odor passed over, but it was obtained in so small quantity that no attempt was made to find out what it was.

The decomposition of the tetrazonium chloride with the alcohols in the presence of zinc dust furnishes a very satisfactory method for the preparation of *m*-ditolyl. The manipula-

tion is very simple and the yield excellent. Heretofore there have been three methods for its preparation:

1. Heating *o*-dicresol with zinc powder.

2. Conversion of dichlor-*m*-ditolyl into *m*-ditolyl by sodium amalgam in alcoholic solution, sodium in solution in amyl alcohol or zinc and hydrochloric or acetic acid.

3. By the action of nitrous acid on an alcoholic solution of *o*-tolidine. This method was discovered by Schultz and used by him and Stolle in their investigations on *m*-ditolyl, being the most satisfactory and economical method of the three. The yields of *m*-ditolyl, as given by these investigators, were never as much as 25 per cent of the theoretical amount.

Several subsequent experiments of mine have shown that a very satisfactory, and perhaps the most useful, method for the preparation of *m*-ditolyl is the decomposition of tetrazonium chloride with ordinary 98 per cent alcohol in the presence of zinc dust, the separation of the *m*-ditolyl being accomplished as described above. A yield of 75 per cent of *m*-ditolyl can be very easily obtained in this way.

Oxidation of m-Ditolyl.—According to Schultz and Stolle, when *m*-ditolyl is oxidized with potassium bichromate and sulphuric acid, the product is isophthalic acid. I attempted to reach this result by using the proportions generally used in such cases, and the acid diluted with 2 volumes of water. After boiling several hours the oxidation had taken place only very slightly. It was found that this oxidation is best effected by using acid diluted to just half its volume with water and about six times the calculated amount of potassium bichromate. The oxidation proceeds smoothly after the first violent reaction is over. After two hours' boiling of the mixture the oxidation is practically completed. After cooling, the solid was filtered off, washed with cold water, dissolved in a dilute solution of sodium carbonate, and the solution of the sodium salt formed decolorized with animal charcoal. On the addition of hydrochloric acid the isophthalic acid was precipitated perfectly white. This was crystallized from water and its melting-point taken. The yield of isophthalic acid by this method was very good. Five grams of *m*-ditolyl were dis-

solved in glacial acetic acid and the calculated amount of chromic acid for its total conversion to diphenyldi-*m*-carboxylic acid was added, this, also, in acetic acid solution. The action was quite violent at first, but soon moderated. This solution was then poured into a flask attached to a reflux-condenser and boiled for several hours. Most of the acetic acid was then distilled off and water added, when a slight precipitation of the desired acid resulted, which was filtered, washed with water, and recrystallized until the melting-point became constant. The acid melts at 190°.5. For the oxidation of *m*-ditolyl, in repetition of Perrier's work, with nitric acid (sp. gr. 1.14), four days were necessary, the acid being boiled continually. On cooling, a white substance separated which was dissolved in a dilute solution of sodium carbonate, precipitated with hydrochloric acid, and recrystallized from a water-alcohol mixture. It was recognized by its melting-point (202°) as the acid obtained by Perrier.

It was thought advisable to try the action of potassium permanganate as an oxidizing agent on *m*-ditolyl, but this powerful reagent was unable to overcome the resistance of this hydrocarbon to oxidation. A neutral solution of the permanganate was first used, but no oxidation resulted. The action of the permanganate was next tried in potassium hydroxide solutions of many concentrations, but the *m*-ditolyl was never oxidized. This oxidation was attempted at the temperature of the boiling-point of water. A slight addition of the permanganate gave the solution a color which hours of heating, in contact with the hydrocarbon, did not remove. *m*-Ditolyl resists most strongly all oxidizing agents. The only one which gave good results was a mixture of potassium bichromate and sulphuric acid, which oxidizes the hydrocarbon to isophthalic acid.

Action of Normal Propyl Alcohol on the Tetrazonium Chloride.—The tetrazonium compound was decomposed with propyl alcohol under different conditions. In the first case, 13 grams of the tetrazonium compound were placed in a small flask and 200 cc. of the alcohol added. The flask was attached to a return-condenser and heated in a water-bath, in

which the water was briskly boiling. It was afterwards found best to heat the flask, placed on a wire gauze and attached to a return-condenser, with a small flame until the reaction begins. The flame is then removed and the reaction proceeds smoothly, the heat generated thereby being almost sufficient to carry it to completion. A little further heating completes the reaction and clears the solution up to a wine color. From 13 grams of the tetrazonium compound a little over 3 grams of *m*-ditolyl, or 40 per cent of the theoretical amount, were obtained. Other experiments showed that the yield of the *m*-ditolyl by this method was at least 45 per cent of the theoretical amount.

Eleven grams of the tetrazonium compound were decomposed in exactly the same manner, except that 10 grams of zinc powder were added. The decomposition was rather more energetic than before, the solution clearing up at the end of the operation to an amber color. On filtering off the zinc dust and evaporating the alcohol a dark-colored oil was left, and as in all cases in which zinc dust had been used, there was a total absence of the formation of any tarry products. The oil remaining was taken up in ether, dried with calcium chloride, and distilled. A little less than 4 grams of *m*-ditolyl were thus obtained, or a yield of at least 60 per cent of the theoretical amount.

The addition of sodium hydroxide to the propyl alcohol caused the decomposition to take place at room temperature very rapidly. Tarry products were formed in abundance, and the reaction that took place was the "hydrogen" one, though the yield was not good.

In none of the decompositions with propyl alcohol did the "alkoxy" reaction take place at all. The "hydrogen" reaction, and that alone, takes place when tetrazo-*m*-ditolyl chloride is decomposed with propyl alcohol.

Preparation of Diphenyltetrazonium Chloride.—The benzidine hydrochloride used in these experiments was prepared thus: One hundred grams benzidine were mixed with 600 cc. water in a large evaporating dish and the mixture heated almost to the boiling-point of water. Hydrochloric acid was

now added in slight excess when all the benzidine dissolved, forming a red solution. This was easily decolorized by animal charcoal. To the colorless solution about one-fourth of its volume of strong hydrochloric acid was added with stirring, when the *p*-benzidine hydrochloride was precipitated in the form of a colorless, fine, crystalline mass. The hydrochloride obtained by this method is almost perfectly pure, as the hydrochlorides of the isomeric benzidines remain in solution. This was filtered off as dry as possible with the aid of a Büchner funnel and filter-pump, and was then, while still slightly moist, bottled and used in that condition, as this was found to be favorable for the formation of the tetrazonium compound.

As in the diazotization of tolidine hydrochloride, a paste of the salt and water was used. In this case it was found more necessary to keep the paste of the hydrochloride and water at a low temperature than was the case with tolidine hydrochloride. To accomplish this the oxides of nitrogen, formed in the usual manner, were passed through a Woulff's bottle, and then the cooled gases were led into a cylinder, which contained the paste of the benzidine hydrochloride and water, and was surrounded with ice. In order to diazotize the hydrochloride completely, about 3 parts of water are necessary to 1 of the salt. For the precipitation of the tetrazonium compound, six times the volume of the water solution of the tetrazonium compound of ordinary alcohol is required. This is previously cooled to as low a temperature as a freezing-mixture can cool it, and poured into the solution. A precipitation in the form of beautiful needles at once takes place. The vessel containing this mixture is then allowed to stand in the freezing-mixture for some time and the tetrazonium compound is then filtered off. If the diazotization has been successful and the water solution is of a light straw color, as it should be, the crystals of the tetrazonium chloride are almost perfectly white. Unfortunately, even if one works with the greatest care, this result is not generally reached, but if attention is paid especially towards keeping the temperature of the paste which is being diazotized below

5°, and the alcohol for precipitation is cold, a good quality of tetrazonium compound will be obtained. The diazotization is best effected by means of a rapid current of the oxides of nitrogen, and, indeed, this is necessary for a successful operation, which is best carried through in from twenty to twenty-five minutes. My early attempts at making this tetrazonium compound were failures, because the current of gases was too slow and the operation took too long a time. Diphenyltetrazonium chloride is a rather heavy substance, settling rapidly to the bottom of the beaker in which it is formed. When it is filtered, washed with alcohol and ether, and dried, it can be handled safely, although it is not as stable a compound as ditolyltetrazonium chloride. The yield of the diazo compound by this method is about 85 per cent of the theoretically possible amount. The change of color during diazotization is not so marked as in the case of the diazotization of tolidine hydrochloride. When the gases are first passed into the mixture a slightly brownish discoloration takes place, which increases slowly until the end of the operation. Then it clears up to a light-yellow, when the operation proceeds best. The greatest care is necessary in keeping all of the solutions, at every stage of the operation, at a low temperature. An important point of difference between *m*-ditolyltetrazonium chloride and diphenyltetrazonium chloride is observed when the two are allowed to stand in contact with alcohol at room temperature. The former is decomposed very slowly, while the latter is easily decomposed, especially if the alcohol is largely diluted with water, in which case tarry products are largely formed. If the same decomposition is effected at the boiling-point of the alcohol the reaction is much cleaner.

Action of Methyl Alcohol on Diphenyltetrazonium Chloride.— Twenty grams of the tetrazonium compound were placed in a 2-liter flask and 300 cc. of absolute methyl alcohol poured over the salt. If this mixture is allowed to stand, gradual decomposition will ensue, but the action will be incomplete and results unsatisfactory. The amount of tarry matter formed will be much larger than if the decomposition is carried on at a higher temperature. When the flask containing the mixture

of the tetrazonium salt and alcohol is attached to a reflux condenser and heated on a water-bath the reaction is very satisfactory, provided certain precautions are taken. There will be little evolution of nitrogen until the boiling-point of the alcohol is almost reached. As soon as the evolution of nitrogen begins the flame should be removed and the action quickened by shaking the contents of the flask. The reaction proceeds smoothly. When the evolution of nitrogen almost ceases, the mixture is heated to boiling for fifteen minutes to complete the reaction. The resulting solution is of a light reddish color and the reaction is quite clean. The methyl alcohol is then distilled off and 6 volumes of a saturated solution of sodium chloride added to the distillate, when the solution becomes slightly cloudy. This was shown to be due to a trace of diphenyl, formed in the reaction. After distillation of the methyl alcohol there remains in the flask a yellow solid, which seems to contain very little matter of a tarry nature. This is broken up, a little water added, and distillation with steam carried on, when a nearly inappreciable amount of a white solid, melting at 68°, is carried over by the steam, which by its melting-point and odor is recognized as diphenyl. The yellow solid remaining in the flask, which is not volatile with water vapor, is then dissolved in ordinary alcohol, in which it is difficultly soluble at its boiling temperature and insoluble in the cold. As in the case of the two phenol ethers, which have already been described, this substance shows a marked difference in its solubility in alcohol at its boiling temperature, and a few degrees below that temperature. The alcoholic solution was then decolorized by boiling with animal charcoal for a few minutes, and on cooling, beautiful plates of a pearly luster were obtained. In this first experiment the yield was 8 grams. When the substance was a second time crystallized the melting-point was sharp at 172°.

Two analyses gave the following results :

I. 0.2000 gram substance gave 0.5775 gram CO_2 and 0.1193 gram H_2O.

II. 0.2000 gram substance gave 0.5751 gram CO_2 and 0.1181 gram H_2O.

	Calculated.	Found. I.	II.
C	78.50	78.75	78.43
H	6.54	6.62	6.56
O	14.96	....	....

The yield of diphenyl, by the action of methyl alcohol on the tetrazonium salt, is very small. The reaction that takes place is the "alkoxy." The largest yields obtained range from 65 to 70 per cent of the theoretical. Dimethoxydiphenyl is insoluble in water, difficultly soluble in alcohol and ether. In alcohol it is not as soluble as are dimethoxy- and diethoxy-*m*-tolyl.

Decomposition of Diphenyltetrazonium Chloride with Methyl Alcohol under Different Conditions.—Sixteen grams of the tetrazonium salt were placed in a flask and 250 cc. methyl alcohol added. Fifteen grams of zinc dust were now introduced and the tetrazonium compound decomposed in the usual way. The decomposition began when the alcohol had almost reached its boiling temperature. It then proceeded smoothly, as in the preceding experiment. The flame was removed as soon as the reaction began, and the heat generated by the reaction was almost sufficient to complete it. In order to be perfectly sure that the reaction was complete, the solution was boiled for a few minutes. The yellow solution resulting was now filtered to remove the zinc dust and the alcohol was distilled off. A portion of the distillate was treated with 6 volumes of a standard solution of sodium chloride, but only a slight precipitation resulted. After this the alcoholic distillate was not treated with sodium chloride, but was preserved for use in other decompositions, as the phenol ether is not volatile with alcohol vapor, and diphenyl only to a very small extent. In this experiment 6.5 grams diphenyl, or 73 per cent of the theoretical yield, were obtained. The brownish residue in the distillation-flask was dissolved in alcohol and carefully examined for dimethoxydiphenyl, but none was found. During the decomposition a strong odor, resembling that of aldehyde, was noticed. As in all other decompositions recorded in which zinc dust was used, the reaction was

practically clean and the presence of the zinc dust determined the "hydrogen" reaction.

Decompositions of diphenyltetrazonium chloride with sodium methylate and with methyl alcohol in the presence of sodium hydroxide were also carried out, but only small amounts of the compound were thus decomposed, the object being simply to find out which way the reaction takes place. The decompositions proceeded in exactly the same way in both cases. In both cases diphenyl was formed. No dimethoxydiphenyl was obtained. The "hydrogen" reaction takes place when diphenyltetrazonium chloride is decomposed with methyl alcohol in the presence of zinc dust, sodium methylate, or sodium hydroxide.

Action of Nitric Acid on Dimethoxydiphenyl.—The best yield was obtained by the use of fuming nitric acid. The product crystallizes from alcohol in beautiful, straw-colored needles, which melt sharply at 244°.6. Three determinations of nitrogen gave as the percentage of that element in the substance 14.6, 14.1, and 14.5, which agree quite well with the formula $C_{14}H_{10}O_2(NO_2)_4$, for which the percentage of nitrogen is 14.22.

Action of Diphenyltetrazonium Chloride on Ethyl Alcohol.—Twenty-three grams of the tetrazonium salt were placed in a 2-liter flask and 300 cc. of absolute ethyl alcohol poured over it. The flask was then attached to a reflux-condenser and heated on a water-bath. The heating of this mixture for the decomposition of the tetrazonium compound requires the greatest care, and special precautions must be taken. Near at hand, a water-bath containing cold water, is placed. The mixture is well shaken while the heating is going on and carefully watched. The reaction does not begin until the boiling temperature of the alcohol is almost reached. As soon as evidences of decomposition are observed the flame is removed, the water-bath containing hot water is taken away. The mixture is now shaken and the decomposition proceeds rapidly. When it increases in violence, the flask is plunged in the cold water and kept there until the action moderates, when it is removed. These operations are repeated until the reaction is over and

all of the compound has gone into a reddish-yellow solution. This is then heated and the alcohol boiled for a few minutes. Throughout the operation the strong odor of aldehyde is noticeable, and it is evident that the reaction that takes place is to a large extent the "hydrogen" one. The first decompositions of this tetrazonium chloride with ethyl alcohol were carried on in the same manner as those with methyl alcohol, and the violence of the reaction was so great that the greater part of the reacting mixture was projected through the condenser-tube across the room. In several subsequent experiments, in which the special precautions were not observed, a considerable loss was occasioned by the same violence. The method described above is that by which the best results were obtained. In the experiment described, the red solution of the decomposition-products was subjected to distillation and all of the alcohol removed in this way. A reddish oil remained, which, on cooling, solidified to a reddish, crystalline mass. The alcoholic distillate was tested by adding to it several volumes of a saturated solution of sodium chloride, when a small quantity of a white solid was precipitated. The rest of the alcohol was not treated in the same way, because the substance was only slightly volatile with alcohol vapor, but was preserved for other decompositions. The reddish residue in the distillation-flask was distilled in steam, and most of it passed over with the water vapor as a white, crystalline solid, having the strong odor of diphenyl and melting, when crystallized from alcohol, at 68°.

The yield was 10.25 grams, or over 80 per cent of that theoretically possible.

I. 0.2000 gram substance gave 0.6841 gram CO_2 and 0.1179 gram H_2O.

II. 0.2000 gram substance gave 0.6825 gram CO_2 and 0.1171 gram H_2O.

	Calculated.	Found. I.	Found. II.
C	93.51	93.30	93.07
H	6.49	6.55	6.50

Thus it is seen that the substance formed by the action of

diphenyltetrazonium chloride on ethyl alcohol is diphenyl, and that the "hydrogen" reaction alone takes place in this case. As benzidine is easily obtained, and these reactions take place easily, this furnishes the best method at present known for the preparation of diphenyl.

Decomposition of Diphenyltetrazonium Chloride with Ethyl Alcohol under Different Conditions.—As in the decompositions described, extreme care was necessary to prevent the reaction from taking place with too much violence. Decompositions were carried on with absolute, 95 per cent alcohol, and alcohol still more dilute in the presence of zinc dust, which was added in about the same amount as the tetrazonium compound. It was found that, as long as the alcohol did not contain more than 15 per cent of water, the decompositions proceeded like those with absolute ethyl alcohol alone. Under proper conditions the reaction was smooth and the decomposition perfectly clean, no tarry products being formed, and the solution clearing up at the end of the operation to a straw color. The zinc powder was now removed by filtration, the yellow solution decolorized with animal charcoal, and evaporated until crystallization took place. Diphenyl was obtained perfectly pure by recrystallizing this product from ordinary alcohol. The yield by this method is from 80 to 85 per cent of the theoretical amount. When the alcohol contains more water than 15 per cent, tarry products are formed, the amount being greater the greater the dilution of the alcohol, and the amount of diphenyl relatively smaller. Sodium hydroxide, added to ethyl alcohol, used for the decomposition of diphenyltetrazonium chloride, causes a violent reaction to take place at room temperature, and a freezing-mixture is required to keep the reaction within bounds. A large amount of tarry products separates, and the diphenyl is removed by distilling off the alcohol and distilling the tarry residue in steam. For a laboratory method for the preparation of diphenyl, I would suggest the decomposition of diphenyltetrazonium chloride with ordinary alcohol in the presence of zinc dust. In all cases in which the tetrazonium chloride was decomposed with ethyl alcohol diphenyl alone was formed.

Action of Normal Propyl Alcohol on Diphenyltetrazonium Chloride.—Twelve grams of the tetrazonium chloride were placed in a half-liter flask and 150 cc. of propyl alcohol added. At room temperature there was practically no action, although when the mixture was allowed to stand for several hours the alcohol became colored reddish. The flask was attached to a reflux-condenser and the alcohol heated to its boiling temperature with a small flame. As soon as the decomposition began the flame was removed and the decomposition allowed to proceed. When the nitrogen almost ceased being given off, the alcohol was boiled for a few minutes and then distilled off. There remained a brownish residue, which was subjected to distillation in steam. A little over 3 grams of diphenyl were thus obtained. This experiment, repeated many times, showed that the yield of diphenyl was between 40 and 50 per cent of the theoretical. When the steam distillation was completed some tarry matter remained in the flask, from which nothing of value was ever obtained. When the tetrazonium compound was decomposed with propyl alcohol in the presence of an excess of zinc dust, the reaction took place in the same manner, but was much cleaner, and the amount of tarry products smaller. By this method the yield of diphenyl was brought up to 60 per cent of the theoretical. The addition of sodium hydroxide to the propyl alcohol used for this decomposition caused the reaction to take place at room temperature and diphenyl was formed, together with much tarry matter. As was found in the case of the decomposition of ditolyltetrazonium chloride with propyl alcohol, so in the case of the decomposition of diphenyltetrazonium chloride with the same alcohol, the "hydrogen" reaction alone took place.

Summary of Experimental Work.

Ditolyltetrazonium chloride, when decomposed with methyl alcohol, yields as the only product dimethoxy-*m*-ditolyl, or the "alkoxy" reaction alone takes place:

$$C_{14}H_{12}N_4Cl_2 + 2CH_3OH = C_{14}H_{12}(OCH_3)_2 + 2N_2 + 2HCl.$$

When the same tetrazonium compound is decomposed with

ethyl alcohol the products of the reaction are *m*-ditolyl and diethoxy-*m*-ditolyl, and these products are formed in approximately equal amounts, or both the "alkoxy" and the "hydrogen" reactions take place:

$$C_{14}H_{12}N_4Cl_2 + 2C_2H_5OH = C_{14}H_{12}(OC_2H_5)_2 + 2N_2 + 2HCl;$$
$$C_{14}H_{12}N_4Cl_2 + 2C_2H_5OH = C_{14}H_{14} + 2C_2H_4O + 2N_2 + 2HCl.$$

When the same tetrazonium compound is decomposed with normal propyl alcohol the only product isolated was *m*-ditolyl, or the "hydrogen" reaction alone takes place:

$$C_{14}H_{12}N_4Cl_2 + 2C_3H_7OH = C_{14}H_{14} + 2C_3H_6O + 2N_2 + 2HCl.$$

When the same tetrazonium compound was decomposed with a solution of sodium methylate in methyl alcohol, the "hydrogen" reaction alone took place. The same reaction was found to take place when the tetrazonium compound was decomposed with each alcohol, in turn, in the presence of sodium hydroxide or zinc powder.

When diphenyltetrazonium chloride is decomposed with methyl alcohol the product is dimethoxydiphenyl, and at the same time a trace of diphenyl is formed, the "alkoxy" reaction taking place almost exclusively:

$$C_{12}H_8N_4Cl_2 + 2CH_3OH = C_{12}H_8(OCH_3)_2 + 2N_2 + 2HCl.$$

The decomposition of the same tetrazonium compound with ethyl alcohol gives only diphenyl, or the "hydrogen" reaction alone takes place:

$$C_{12}H_8N_4Cl_2 + 2C_2H_5OH = C_{12}H_{10} + 2C_2H_4O + 2N_2 + 2HCl.$$

The same tetrazonium compound, decomposed with normal propyl alcohol, yields only diphenyl or the "hydrogen" product:

$$C_{12}H_8N_4Cl_2 + 2C_3H_7OH = C_{12}H_{10} + 2C_3H_6O + 2N_2 + 2HCl.$$

Sodium methylate, in methyl alcoholic solution, yields only diphenyl.

When the tetrazonium compound is decomposed with methyl, ethyl, or propyl alcohol in the presence of sodium hydroxide, or zinc powder, the "hydrogen" reaction alone takes place.

SOME Δ_3-KETO-R-HEXENE DERIVATIVES.

By James B. Garner.

A study of the reactions which might be brought about between benzoin and unsaturated aldehydes, ketones, and esters through the agency of cold (15° C.) alcoholic sodium ethylate, was begun several years ago.[1] At that time it was found that benzoin is added to benzalacetone giving rise to a 1,5-diketone which, by loss of water and ring formation, is converted into 3,4,5-triphenyl-4-oxy-Δ_3-keto-R-hexene. This substance had previously been prepared by Professor Alexander Smith,[2] using potassium cyanide as condensing agent.[3] When sodium ethylate is used as condensing agent, the yield is much greater, the reaction takes place more smoothly, and the product formed is purer than when potassium cyanide is used. Knovenagel has made an exhaustive study of the Δ_3-keto-R-hexene derivatives. He has found (1) that substances of the type of acetoacetic ether and aliphatic aldehydes,[4] and aromatic aldehydes,[5] condense in the presence of diethylamine or piperidine to form 1,5-diketones, and that these diketones, with loss of water and ring formation, are converted into Δ_3-keto-R-hexene derivatives; (2) that desoxybenzoin adds itself to substances of the type benzalacetylacetone, forming 1,5-diketones, which, by loss of water and ring formation, yield Δ_3-keto-R-hexene derivatives.

Recently the study has been extended to include the reactions which might take place between the ketols—benzoin, cuminoin, furoin, anisoin, and piperonoin—and the unsaturated ketones—benzalacetone, cuminalacetone, *p*-methoxybenzalacetone, and piperonylenacetone. In all the reactions, Δ_3-keto-R-hexene derivatives are formed, except in those in which furoin is used. Under no conditions has it been possible to bring about any interaction in any of the experiments in which furoin is used. All of the other reactions progress smoothly and excellent yields are obtained in each case. It

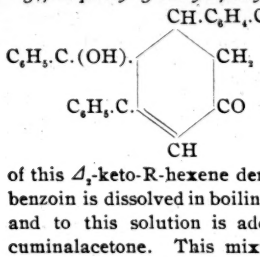
[1] Dissertation, Chicago, 1897, p. 17.
[2] Ber. d. chem. Ges., **26**, 65.
[3] This Journal, **22**, 250.
[4] Ann. Chem. (Liebig), **281**, 25; *Ibid.*, **288**, 321.
[5] *Ibid.*, **306**, 223.

has been ascertained also, that in place of the unsaturated ketone a mixture of the corresponding aldehyde and acetone may be used and the course of the reaction is in no way changed, but the yield is materially increased. To insure the completion of the reactions, however, it is necessary to boil the mixtures for fifteen minutes on the water-bath. An equal volume of a 10 per cent solution of sodium hydroxide may be used instead of the alcoholic sodium ethylate and the same reactions will take place but the yields are poorer.

In the present paper the study is limited to the consideration of only those cases which will, in a general way, indicate, (1) the nature of the products formed; and (2) the extent to which the reaction is applicable.

I. Addition of Benzoin to Cuminalacetone.

3,4-Diphenyl-5-cumyl-4-oxy-Δ_2-keto-R-hexene,



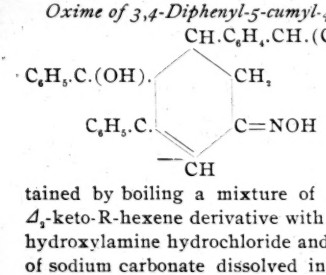
.—For the preparation of this Δ_2-keto-R-hexene derivative, 1 molecule (6 grams) of benzoin is dissolved in boiling absolute ethyl alcohol (100 cc.), and to this solution is added 1 molecule (5.32 grams) of cuminalacetone. This mixture is treated with an alcoholic solution (4 cc.) of sodium ethylate (0.5 gram sodium in 30 cc. absolute ethyl alcohol). The mixture becomes deep-red in color, and upon standing in a cool place for two days deposits clusters of needle-like crystals. The crystalline mass is filtered off and after washing with absolute ethyl alcohol is recrystallized twice from glacial acetic acid. Clusters of long, fine, white needles result, which melt at 231°. It is insoluble in ligroin (40°–60°), ether, and cold alcohol, but dissolves readily in hot benzene, glacial acetic acid, and chloroform.

	Calculated for $C_{31}H_{28}O_2$.	Found.
C	84.80	84.67
H	6.81	6.92

If a mixture of one molecule each of cuminol (4.2 grams) and pure acetone (1.7 grams) is used instead of the cuminal-acetone, it has been established by several comparable experiments that it is necessary that the reaction shall be carried on at the temperature of the water-bath for fifteen minutes. Upon cooling the mixture, the Δ_2-keto-R-hexene derivative separates in a relatively pure condition. By repeated additions of 4 cc. of sodium ethylate at a time, additional quantities of the substance are obtained which make the yield almost quantitative. Experiments were made using the total quantity of sodium ethylate solution (12 cc.) required for the quantitative completion of the reaction, and it was found that the reaction took an entirely different course, resulting in the formation of the sodium ethylate addition-product of benzoin.[1]

The condensation takes place readily when 15 grams of a 10 per cent solution of sodium hydroxide are used in place of the 4 cc. of sodium ethylate solution.

Oxime of 3,4-Diphenyl-5-cumyl-4-oxy-Δ_3-keto-R-hexene,

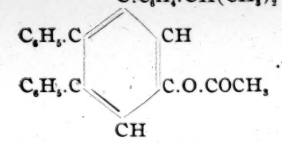


.—This oxime is obtained by boiling a mixture of 1 molecule (1 gram) of the Δ_3-keto-R-hexene derivative with 3 molecules (0.56 gram) of hydroxylamine hydrochloride and 1.5 molecules (0.56 gram) of sodium carbonate dissolved in ethyl alcohol (140 cc.) for forty-five minutes, using a return-condenser. One-half of the alcohol is distilled off and the residue, on cooling, deposits white crystals, which, when they have been recrystallized from a mixture of benzene and ligroin, melt at 221° to 223°. The substance is easily soluble in hot alcohol, cold ether, acetic acid, and hot benzene, but very sparingly soluble in hot ligroin (40° to 60°).

	Calculated for $C_{27}H_{27}O_2N$.	Found.
N	3.53	3.72

[1] Dissertation, Chicago, 1897, p. 4.

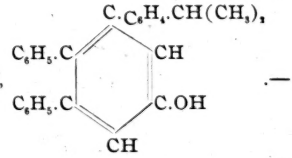
3,4-Diphenyl-5-cumylphenol Acetate,



.—This body is prepared by boiling the Δ_2-keto-R-hexene derivative with excess of either acetic anhydride or acetyl chloride for thirty minutes. The mixture assumes a yellowish-red tint, and yields a solid substance only when it is poured into a large excess of water. The white, amorphous mass recrystallizes from hot ligroin (40° to 60°) in bunches of long needles, melting at 98°. It is soluble in cold glacial acetic acid, benzene, ether, and alcohol, but is sparingly soluble in ligroin.

	Calculated for $C_{29}H_{28}O_2$.	Found.
C	85.72	85.50
H	6.40	6.62

3,4-Diphenyl-5-cumylphenol,

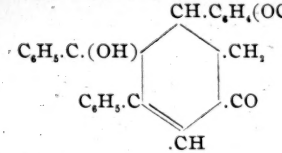


.—The acetate is boiled upon a water-bath with alcoholic potassium hydroxide for fifteen minutes. The mixture resulting is poured into excess of dilute hydrochloric acid, and a white mass is obtained. The amorphous phenol is recrystallized from hot alcohol. It forms white needles, which melt at 155°. It is readily soluble in cold chloroform, benzene, and ether, but sparingly soluble in hot ligroin (40° to 60°).

	Calculated for $C_{27}H_{24}O$.	Found.
C	89.00	88.96
H	6.60	6.87

II. Addition of Benzoin to Anisylideneacetone.

3,4-Diphenyl-5-anisyl-4-oxy-Δ_3-keto-R-hexene,



.—The 3,4-diphenyl-5-anisyl-4-oxy-Δ_3-keto-R-hexene is prepared by the condensation of 1 molecule (6 grams) of benzoin, either with 1 molecule (5 grams) anisylideneacetone or with 1 molecule each of anisaldehyde (3.9 grams) and of pure acetone (1.7 grams) under exactly the same conditions which were used in the preparation of 3,4-diphenyl-5-cumyl-4-oxy-Δ_3-keto-R-hexene. The substance crystallizes in bunches of needles, either from hot glacial acetic acid or absolute alcohol, and melts at 233°.5. However the amount of alcohol required is large—for each gram 70 cc. of hot absolute alcohol are required. It is soluble in hot benzene and chloroform, but insoluble in ether and ligroin (40° to 60°). With cold concentrated sulphuric acid, a deep red coloration is produced.

	Calculated for $C_{28}H_{24}O_3$.	Found.
C	81.08	80.91
H	5.95	6.03

Oxime of the 3,4-Diphenyl-5-anisyl-4-oxy-Δ_3-keto-R-hexene.—For the preparation of the oxime a method, analogous to that described in the preparation of the oxime of 3,4-diphenyl-5-cumyl-4-oxy-Δ_3-keto-R-hexene, is used. After recrystallization from hot alcohol it melts at 196°. It is soluble in hot glacial acetic acid, chloroform, and benzene, but insoluble in ether and ligroin (40° to 60°).

	Calculated for $C_{28}H_{25}O_3N$.	Found.
N	3.63	3.85

Acetate of 3,4-Diphenyl-5-anisylphenol—This product is obtained by boiling the Δ_3-keto-R-hexene derivative with acetyl chloride on the water-bath for ten minutes. The mixture as-

sumes a deep red coloration. Nothing separates on cooling. When excess of water is added, however, an amorphous mass separates which, upon crystallization from hot ligroin (40° to 60°) or from aqueous alcohol, melts at 141° to 142°. It is soluble readily in cold benzene, ether, glacial acetic acid, and chloroform; sparingly soluble in hot benzene and aqueous alcohol.

	Calculated for $C_{27}H_{22}O_3$.	Found.
C	82.22	82.10
H	5.59	5.84

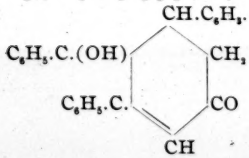
3,4-Diphenyl-5-anisylphenol.—The acetate, upon saponification with alcoholic potassium hydroxide, yields the phenol. The reaction requires only fifteen minutes' heating upon the water-bath to complete it. The product, which is obtained when the resulting solution is poured into dilute hydrochloric acid, is recrystallized from a mixture of alcohol and ligroin (40° to 60°) and melts at 159° to 160°. It is readily soluble in cold ether, benzene, chloroform, and acetic acid, and almost insoluble in hot ligroin.

	Calculated for $C_{25}H_{20}O_2$.	Found.
C	85.24	85.17
H	5.68	5.93

This phenol reacts vigorously at the ordinary temperature with cold concentrated nitric acid and yields nitro derivatives. These nitro bodies will be investigated later.

III. Addition of Benzoin to Piperonyleneacetone.

3,4-Diphenyl-5-piperyl-4-oxy-Δ_2-keto-R-hexene,



.—One molecule (6 grams) of benzoin and 1 molecule of piperonyleneacetone are dis-

solved in hot absolute ethyl alcohol (100 cc.) and a solution (4 cc.) of sodium ethylate (0.5 gram sodium in 30 cc. absolute alcohol) is added. As in all these condensation-reactions with sodium ethylate, this mixture assumes a deep red coloration. Upon standing for two hours, rosettes of yellow, needle-like crystals separate. These crystals, upon recrystallization from glacial acetic acid, are obtained in fine, white, glittering needles, melting at 240°. The substance is soluble in hot chloroform; sparingly soluble in hot benzene and alcohol; and insoluble in ether and ligroin (40° to 60°).

	Calculated for $C_{28}H_{20}O_4$.	Found.
C	78.12	78.00
H	5.21	5.35

The method above described for the preparation of 3,4-diphenyl-5-piperyl-4-oxy-Δ_3-keto-R-hexene does not progress as smoothly and as completely as when 1 molecule each of piperonal (4.25 grams) and of pure acetone (1.7 grams) is used in place of the piperonyleneacetone, and the reaction is carried out at the temperature of the water-bath. The crystals obtained by this method are very pure and clean, and the yield is almost quantitative, especially if the mother-liquor is treated again with more sodium ethylate and the mixture again boiled.

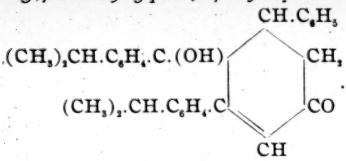
Ten per cent sodium hydroxide solution also effects the condensation. However, the yield is poor.

Oxime of 3,4-Diphenyl-5-piperyl-4-oxy-Δ_3-keto-R-hexene.—This oxime is prepared in an analogous method to that described previously for the preparation of oximes. When recrystallized from a mixture of alcohol and ligroin, crystals are formed melting at 190° to 191°. It is soluble in hot alcohol, cold ether, chloroform, and hot benzene, and is insoluble in ligroin (40° to 60°).

	Calculated for $C_{28}H_{21}O_4N$.	Found.
N	3.51	3.78

IV. Addition of Cuminoin to Benzalacetone.[1]

3,4-Dicumyl-5-phenyl-4-oxy-Δ_2-keto-R-hexene,



.—Cuminoin, in general, reacts less rapidly than benzoin, and the yields of Δ_2-keto-R-hexene derivatives are poorer.

One molecule (6 grams) of pure cuminoin[2] and 1 molecule (3 grams) of pure benzalacetone dissolved in hot absolute ethyl alcohol (60 cc.) are treated with a solution (6 cc.) of sodium ethylate (0.5 gram sodium in 30 cc. absolute alcohol). Upon the addition of the sodium ethylate, the mixture turns deep red, and, after standing for six hours, clusters of needles separate. By recrystallizing twice from glacial acetic acid, pure 3,4-dicumyl-5-phenyl-4-oxy-Δ_2-keto-R-hexene is obtained. It melts at 214°. It is soluble in cold acetic ether, chloroform, hot benzene, and ligroin (110° to 120°); insoluble in cold alcohol, ligroin (40° to 60°), and ether. The yield is about 27 per cent of the theoretical.

	Calculated for $C_{30}H_{32}O$.	Found.
C	84.90	84.77
H	7.54	7.83

Oxime of the 3,4-Dicumyl-5-phenyl-4-oxy-Δ_2-keto-R-hexene.—A molecule of the substance dissolved in alcohol was boiled with 3 molecules of hydroxylamine hydrochloride for an hour. On cooling, nothing appeared, but after the larger portion of the alcohol had been distilled off in the water-bath a solid separated, which, on being well washed with water and recrystallized from a mixture of benzene and ligroin (40° to 60°), gave fine, white needles melting at 208°. It may be recrystallized also from aqueous alcohol. The analysis shows it to be the monoxime.

[1] Dissertation, Chicago, 1897, p. 19.
[2] Ber. d. chem. Ges., 26, 64.

	Calculated for $C_{30}H_{33}O_2N$.	Found.
N	3.11	3.30

The substance is easily soluble in cold acetic acid, benzene, and acetic ether; insoluble in ligroin (40° to 60°).

3,4-Dicumyl-5-phenylphenol Acetate.—The body can easily be prepared by boiling the Δ_1-keto-R-hexene derivative with a mixture of acetic anhydride and anhydrous sodium acetate for forty-five minutes, or until the mixture becomes decidedly pink in color. The solution is then poured into a large amount of cold water and allowed to settle. After recrystallization from glacial acetic acid it is obtained in large bunches of long, radiating fibers, and melts, when pure, at 122°. It is soluble in cold benzene, chloroform, ether, and ligroin (40° to 60°), in hot alcohol and acetic acid.

	Calculated for $C_{32}H_{32}O_2$.	Found.
C	85.71	85.60
H	7.14	7.55

The acetyl derivative, when hydrolyzed by means of alcoholic potash, yields 3,4-dicumyl-5-phenylphenol.

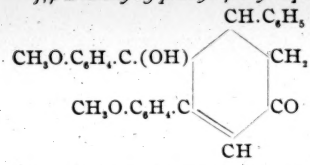
By warming the acetate in a water-bath for ten minutes with four molecules of alcoholic potash and pouring into dilute hydrochloric acid, an amorphous mass is obtained which crystallizes from warm alcohol in large thin plates, melting at 137°. This substance is soluble in cold acetic ether, benzene, chloroform, ether, and hot ligroin (40° to 60°); insoluble in caustic soda.

	Calculated for $C_{30}H_{30}O$.	Found.
C	88.66	88.26
H	7.39	7.99

The addition-reactions of cuminoin with cuminalacetone, piperonyleneacetone, and anisylideneacetone are being studied at present, and I hope to be able soon to publish the results obtained.

V. Addition of Anisoin to Benzalacetone.

3,4-Dianisyl-5-phenyl-4-oxy-Δ_2-keto-R-hexene,



.—Anisoin adds itself to the ethylene grouping much more readily than either cuminoin or benzoin to yield the expected 1,5-diketone, but the readiness with which this 1,5-diketone loses water to form the corresponding Δ_2-ketone-R-hexene derivative is markedly less. In fact, the 1,5-diketone constitutes the major portion of the reaction-product. Attempts to prepare the 1,5-diketone pure, *i. e.*, free from the Δ_2-keto-R-hexene derivatives, have failed partially. However, its approximate melting-point has been obtained, namely, 168° to 174°. When boiled with the ordinary solvents in which it is soluble, the 1,5-diketone loses water and forms the Δ_2-keto-R-hexene derivative, which melts at 207°.

The mixture of the 1,5-diketone and the Δ_2-keto-R-hexene derivative is prepared as follows:

One molecule (4.4 grams) of anisoin and 1 molecule (2.38 grams) of benzalacetone are dissolved in absolute ethyl alcohol (62 cc.) and to the mixture sodium ethylate solution (4 cc.) is added. The solution becomes deep red, and upon standing for two hours deposits a large mass of crystals (2.4 grams). The solid is filtered off and washed well with absolute alcohol. A trial determination of the melting-point shows that the product is a mixture. It melts at 168° to 174° and 204°. The mother-liquor from the crystals, upon treatment with more sodium ethylate solution yields more of the same products (0.4 gram). Upon recrystallization from either of three solvents—benzene, alcohol, or acetic acid—fine, white, needle-like crystals are obtained, having a constant melting-point of 207°. It is soluble in chloroform, slightly soluble in ligroin, and insoluble in ether.

	Calculated for $C_{28}H_{24}O_4$.	Found.
C	78.00	77.62
H	6.00	6.13

The acetate and oxime have been prepared, but as yet no analyses have been made, but the physical properties determined correspond very closely with those of the other Δ_3-keto-R-hexene derivatives which I have prepared.

An investigation of the reaction of anisoin with cuminal-acetone, piperonyleneacetone, and anisylideneacetone is being carried on.

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A NEW METHOD FOR THE DETERMINATION OF FREE LIME AND ON SO-CALLED "DEAD BURNT" LIME.

BY EDWARD H. KEISER AND S. W. FORDER.

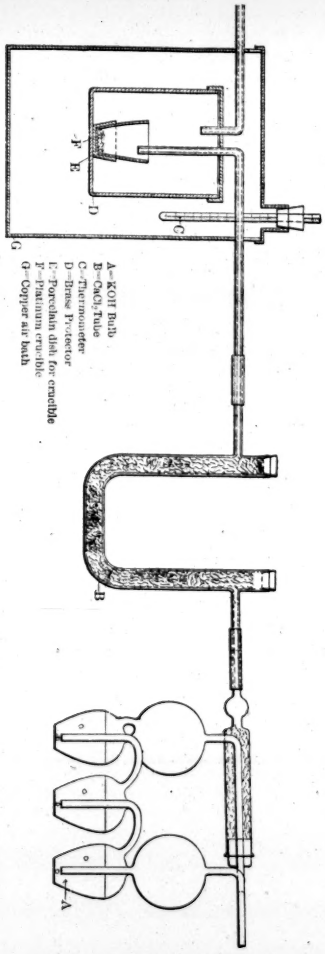
A great many attempts have been made to devise a quantitative method for the determination of free lime in Portland cements, basic phosphate slags, commercial quicklime, and similar substances, but none of the methods thus far proposed has been satisfactory, nor have any of them come into general use. The difficulty is that in the substances mentioned, besides the free lime, there are basic lime compounds, such as the basic di- and tricalcium silicates which are decomposed by water with the formation of calcium hydroxide. When these substances are treated with aqueous solutions, as for example, sugar solution, for the purpose of dissolving the free lime, the water of the solution at once acts upon the basic lime compounds and forms calcium hydroxide. It is, therefore, impossible to determine how much of the lime that is found was in combination and how much was in free condition.

The method described below depends upon the fact that uncombined lime, that is, free lime, combines almost instantly with water, whereas the basic calcium silicates are acted upon much more slowly by water. The process is carried out as

follows: A weighed quantity of the substance, 0.2 to 0.5 gram, is first heated in a platinum crucible to drive off moisture, or in the case of cements, is heated with the blast-lamp for a few minutes to expel any carbon dioxide, and after cooling in a desiccator is again weighed. A few drops of distilled water, which has been recently boiled, are then added and the crucible placed in the brass protector, D, shown in the figure. (D is simply a cylindrical box provided with a screw-top carrying a brass inlet and outlet tube. The thread of the cap is made air-tight with a little white lead and oil.) The protector is put into the air-bath and the temperature is raised to 85° C. and allowed to remain at about this point for thirty minutes. Then a slow current of air is drawn through the apparatus and the temperature raised to 185°. The air is freed from carbon dioxide and moisture by passing through the potash bulb and calcium chloride tube, A and B., as shown in the figure. After drying in this way for thirty minutes the apparatus is disconnected, the protector removed from the air-bath, and the crucible taken out and placed in a desiccator, and when cold is weighed. The increase of weight is the weight of water taken up by the quicklime to form calcium hydroxide.

The method and apparatus were first tested by hydrating pure lime obtained by the ignition of Iceland spar. A weighed quantity of Iceland spar was heated for from five to ten minutes in a platinum crucible with the blast-lamp. After cooling in a desiccator the weight of quicklime was determined. The hydration was then carried out as above described. The following results were obtained:

Weight of lime taken. Gram.	Weight of water absorbed. Gram.	Weight of lime found. Gram.	Lime found. Per cent.
0.2239	0.0724	0.2252	100.60
0.3287	0.1049	0.3263	99.26
0.2368	0.0757	0.2355	99.45
0.2799	0.0909	0.2828	101.00
0.5322	0.1704	0.5300	99.60
0.1579	0.0507	0.1577	99.90
0.1810	0.0581	0.1807	99.88
0.2425	0.0852	0.2433	100.30
0.2487	0.0794	0.2470	99.33



A—KOH Bulb
B—$CaCl_2$ Tube
C—Thermometer
D—Brass Protector
E—Porcelain dish for crucible
F—Platinum crucible
G—Copper air bath

These results show that the method is quantitative and that lime that has been heated to the highest temperature attainable in a platinum crucible with the blast-lamp is completely slaked in twenty minutes at 85°. In fact, in the case of pure quicklime, the slaking is very rapid. The calcium hydroxide was found to be constant in weight up to 250°, beyond which it was not tested. The calcium hydroxide, when exposed to the air, of course, takes up carbon dioxide. It is, therefore, necessary to keep the crucible in a desiccator containing caustic potash instead of calcium chloride, and to weigh as rapidly as possible.

Hydration of Commercial Lime.

For the determination of calcium oxide in commercial quicklime a large piece was taken and the exterior portions broken away and a sample for analysis taken from the interior of the lump. This was quickly placed in a tightly stoppered weighing-tube. Portions of this were weighed off in a platinum crucible and then water was added in a little greater quantity than was necessary for slaking, the crucible put in the protector, warmed to 85° for some minutes, and then a slow current of air free from carbon dioxide drawn through for half an hour, the temperature now being raised to 185°. After cooling in the desiccator, the increase in weight was determined and from this the percentage of lime in the sample calculated. The following results were thus obtained :

Percentage of water.	Percentage of calcium oxide calculated.
29.11	90.56
29.21	90.88
28.98	90.20

This same specimen of quicklime, after ignition over the blast-lamp and immediate hydration, gave the following :

Water taken up. Per cent.	Lime by calculation. Per cent.
32.30	100.50
32.36	100.70

This shows the extent to which the lime had been acted upon by the moisture and carbon dioxide of the air.

The method is also well adapted for rapidly determining the value of limestones for the purpose of making quicklime. Thus a small quantity of the limestone is weighed in a platinum crucible, then ignited with the blast-lamp, and, after weighing, the quicklime is hydrated by this method. From the weight of water taken up the per cent of lime is calculated. The first series of determinations given above shows what results would be obtained with a pure limestone, such as Iceland spar or calcite. The following determinations were made with a siliceous dolomite from Arkansas.

Weight of dolomite. Gram.	Weight of water taken up. Gram.	Percentage of lime.
0.2974	0.0137	14.33
0.2896	0.0134	14.40

Hydration of Dead Burnt Lime.

It is generally believed by practical men that lime that has been very highly heated becomes dead burnt or inert to water. Statements to this effect are found in chemical literature. Thus Dammer[1] states that "very high temperatures must be avoided in the preparation of lime, especially if impure calcium carbonate is used, because the lime at too high temperatures becomes dead burnt, that is, it becomes incapable of uniting with water." Zulkowski[2] maintains that a portion of the lime in Portland cements is in this dead burnt condition. In an article in the Thonindustrie Zeitung, 1902, the same author suggests the formula for dead burnt lime.

For the purpose of determining the behavior of highly heated lime towards water, powdered Iceland spar was placed between the carbon pencils of an electric arc and the current passed for one hour. A number of particles of semi-fused lime were thus obtained. These particles were carefully separated from the powder that had not melted and weighed quantities were hydrated by the above described method. It was found that this lime that had been heated in the electric arc

[1] Handbuch der anorganischen Chemie, II., 2, 294.

[2] Chemische Industrie, 1901, p. 290.

slaked more slowly than that which had not been heated to so high a temperature, but still it combined slowly with water at ordinary temperatures, and on allowing it to stand with water at the ordinary temperature for twenty-four hours it had slaked completely. When the temperature was raised to 85° the slaking was complete in two hours. The following results were obtained:

Weight of lime taken. Gram.	Weight of water taken up. Gram.	Lime calculated from water. Per cent.
0.2799	0.0909	101.0
0.2050	0.0661	100.3
0.5322	0.1704	99.6
0.3909	0.1279	101.0

Another specimen of lime that had been heated with the oxy-coal-gas blow-pipe gave the following result:

Weight of lime. Gram.	Weight of water taken up. Gram.	Percentage of lime.
0.3557	0.1163	100.5

These experiments show that pure lime that has been heated to very high temperatures, even semi-fused lime, is not inert to water and that it slakes comparatively rapidly if the water is warm. That the slaking with cold water is slower than in the case of ordinary lime may be due to the fact that lime that has been heated to very high temperatures is much more compact and less porous than the ordinary lime. The surface exposed to the action of water being much less the time required for slaking would necessarily be greater. We see from these experiments that pure lime cannot be made inert to water by heating to high temperatures. The inertness of commercial lime is probably due to the presence of compounds of silica and iron oxide with the lime which are decomposed very slowly by the water.

Hydration of Calcium Silicates.

The hydration of lime and its compounds was further studied by making synthetically the compounds that are assumed to be present in Portland cement, and then hydrating these substances by this method. Pure lime and silica were

mixed in molecular quantities so as to give, when fused, the compounds, CaO,SiO_2, $2(CaO)SiO_2$, $2\frac{1}{2}(CaO)SiO_2$, $3(CaO)SiO_2$, and $4(CaO)SiO_2$. The lime was obtained by the ignition of pure precipitated calcium carbonate. The silica was prepared by conducting silicon tetrafluoride into water and then drying and igniting the gelatinous silicic acid thus formed. Intimate mixtures of lime and silica in the proportions to form the above compounds were heated by projecting vertically the flame of the oxy-coal-gas blowpipe down upon the mixtures in a cavity made in a fire-brick. The heat thus obtained was sufficient to melt all except the last mixture, namely, the $4(CaO)SiO_2$. The fused masses were in each case carefully separated from the unfused portions, they were chilled by sprinkling with cold water, dried, and preserved in stoppered bottles. Weighed quantities were then hydrated by this method. The hydraulic properties of each compound were also examined by mixing some of the powdered compound with water and observing whether the mass set and became hard. The following table contains the results that were obtained :

Compound.	Hydraulic properties.	Weight taken.	Weight of water taken up.	Percentage of water.	Percentage of lime.
		Gram.	Gram.		
CaO,SiO_2	None	0.4829	0.0004	0.082	0.26
$2(CaO)SiO_2$	Not quite as hard as cement	0.3988	0.0017	0.42	1.33
"	Not quite as hard as cement	0.3997	0.0012	0.30	0.93
$2\frac{1}{2}(CaO)SiO_2$	Not quite as hard as cement	0.4241	0.0022	0.52	1.61
$3(CaO)SiO_2$	Hard as cement	0.4341	0.0044	1.01	3.15
$4(CaO)SiO_2$	None	0.4241	0.0262	6.15	19.15

We conclude from these results that lime in combination with silica in quantities not exceeding 3 molecules of lime for 1 molecule of silica is only slowly acted upon by water and that this method of determining lime can be used to deter-

mine free lime in the presence of the basic di- and tricalcium silicates that are assumed to be present in Portland cements.

Hydration of Calcium Aluminates.

The mono-, di-, and tricalcium aluminates were also prepared synthetically by fusing molecular quantities of pure alumina and lime with the oxy-coal-gas blowpipe flame. The alumina was prepared by heating the hydroxide that had been obtained by precipitation from the chloride with ammonia. The aluminates all fused much more easily than the silicates under the oxy-coal-gas blowpipe. Weighed quantities were hydrated by our method as in the case of the silicates and the hydraulic properties were also noted. It was found that the aluminates differ markedly from the silicates in their behavior towards water. This is shown by the following results:

Compound.	Hydraulic properties.	Weight taken.	Weight of water taken up.	Percentage of water.	Percentage of lime.
		Gram.	Gram.		
$(CaO)Al_2O_3$	Set very hard	0.4886	0.0653	13.34	41.52
$2(CaO)Al_2O_3$	Like a cement	0.4543	0.0716	15.76	49.04
$3(CaO)Al_2O_3$	None	0.4072	0.0796	19.55	60.80

We see from this that the aluminates are hydrated very much more rapidly than the silicates, in fact they behave like free lime when warmed with water to 85° for thirty minutes. In the case of the monocalcium aluminate the percentage of water taken up shows a hydration of the alumina as well as of the lime. It is our intention to make a further study of this part of the subject. In determining free lime, therefore, by this method in substances containing calcium aluminates, this fact must be borne in mind, and the lime in combination with the alumina must be deducted from the total lime found.

Behavior of Cements.

As in commercial cements the proportion of alumina usually varies from 5 to 9 per cent, we have prepared several cements

by fusing with the oxy-coal-gas blowpipe pure alumina, lime, and silica in definite proportions and have then hydrated the resulting cements by our method. The following results were obtained :

Composition of cement.	Hydraulic properties.	Water taken up. Per cent.
5 per cent Al_2O_3	Set slowly, did not become	
25 " SiO_3	quite as hard as Portland	
70 " CaO	cement	1.43
9 " Al_2O_3	Set slowly and became	
21 " SiO_3	quite as hard as Portland	
70 " CaO	cement	2.16
15 " Al_2O_3		
15 " SiO_2	Set slowly and became very	
70 " CaO	hard	4.65

We see from this that as the proportion of alumina increases the percentage of water taken up increases, but if the proportion of alumina does not exceed 10 per cent, as is the rule in commercial cements, then the amount of water taken up does not exceed 3 per cent.

A number of the best known varieties of commercial cements were then examined by our method. In each case the sample was weighed in a platinum crucible, then ignited for a few minutes over the blast-lamp, and after cooling in the desiccator it was weighed. The cement was then moistened with a few drops of water, the crucible put into the protector and warmed to 85° for thirty minutes. Then the temperature was raised to 185° and a slow current of air drawn through until constant weight was obtained. The following results were obtained :

Cement.	Water taken up. Per cent.	Cement.	Water taken up. Per cent.
A	1.16	I	1.81
B	1.97	J	2.99
C	2.09	K	2.77
D	2.67	L	2.18
E	2.88	M	2.61
F	2.66	N	2.64
G	3.01	O	3.04
H	3.10		

These cements all had good, "sound" tests, and in nearly all cases less than 3 per cent of water was taken up. We conclude from this and from the preceding experiments upon cements that this water was taken up by the aluminates and that little or no free lime was contained in these cements. One variety of Portland cement that we examined gave 10.17 per cent of water taken up. We concluded that 7 per cent of this must be due to free lime being present. Our conclusion was justified, for, on making a pat of the neat cement and allowing it to set thoroughly, it was immersed in boiling water, and on removal from the water it showed signs of cracks and had become quite soft and readily disintegrated.

Two varieties of natural cements were tested and gave the following values:

Natural cement.	Water taken up. Per cent.
A	5.76
B	3.70

Finally, we have tested our method by adding weighed amounts of pure lime to a cement of known behavior and then, after ignition with the blast-lamp, have again determined the percentage of water taken up. Thus, cement A, which took up 1.16 per cent of water, had 15.40 per cent of lime added to it. Then, on retesting, it took up 6.25 per cent of water. Percentage of lime corresponding to 1.16 per cent of water, equals 3.60. This, plus the 15.40 per cent added, equals 19.00 per cent. Lime, corresponding to 6.25 per cent of water, equals 19.44.

We conclude from our experiments that if a Portland cement, containing less than 10 per cent of alumina, takes up more than 3 per cent of water, then this excess is due to the free lime present.

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WASHINGTON UNIVERSITY,
ST. LOUIS, Oct., 1903.

SOME ADDITION-REACTIONS OF SULPHINIC ACIDS.

By Elmer P. Kohler and Marie Reimer.

Only two cases of direct union between sulphinic acids and other substances have, so far as we know, been described. Hinsberg[1] found that sulphinic acids combine with quinones and with substances that have a quinoid structure:

$$C_6H_4O_2 + C_6H_5SO_2H = C_6H_4(OH)_2SO_2C_6H_5.$$

Hantsch and Glogauer[2] described sulphonehydrazo compounds which they obtained by direct union between benzenesulphinic acid, and azo and diazo compounds.

We have found that sulphinic acids combine more or less readily with aldehydes, Δ-1,2-unsaturated acids, and Δ-1,2-unsaturated ketones. We did not succeed in getting addition-products with saturated ketones.

The 1,1-oxysulphones obtained by the union of aldehydes and sulphinic acids are very unstable substances. Unless derived from non-volatile aldehydes, they slowly change in the air, even when they are perfectly pure and dry, the aldehyde evaporating while the sulphinic acid undergoes oxidation. In solution, all rapidly dissociate into their components, hence they can be kept only in the presence of a considerable excess of one of the constituents. This explains why these substances cannot be obtained by the action of alkalies on the halogen substitution-products of sulphones.[3]

When a sulphinic acid combines with an α,β-unsaturated acid or an α,β-unsaturated ketone the sulphone group invariably goes into the β-position. The resulting products are stable substances which crystallize well and which can be used for identifying minute quantities of unsaturated ketones. They are very sensitive to alkalies, which smoothly split off the sulphinic acid and regenerate the unsaturated compound. This behavior may explain the fact that only 1,2-disulphones are easily hydrolyzed by alkalies. The hydrolysis is probably the result of two successive processes:

[1] Ber. d. chem. Ges., **27**, 3259.

[2] *Ibid.*, **30**, 2548.

[3] Fromm: Ann. Chem. (Liebig), **253**, 135.

$$\text{I.}\quad \begin{matrix}CH_2SO_2R\\ |\\ CH_2SO_2R\end{matrix} + KOH = \begin{matrix}CH_2\\ \|\\ CH_2SO_2R\end{matrix} + RSO_2K;$$

$$\text{II.}\quad \begin{matrix}CH_2\\ \|\\ CHSO_2R\end{matrix} + \begin{matrix}OH\\ |\\ H\end{matrix} = \begin{matrix}CH_2OH\\ |\\ CH_2SO_2R\end{matrix}.$$

Ketones that have two double linkages in the α,β-position combine in the cold, with one molecule of a sulphinic acid. The resulting unsaturated sulphones combine with bromine, but all efforts to add a second molecule of a sulphinic acid were fruitless.

The ease with which sulphinic acids combine with unsaturated ketones and the stability of the resulting sulphones led us to study some ketones which contain the grouping that Thiele has called "a conjugated system of vicinal double unions."[1] We found that these ketones combine, in the cold, with 1 molecule of a sulphinic acid, and that the addition takes place at the double linkage nearest the carbonyl group, the sulphone group going into the β-position.

The study of sulphinic acids has led to the discovery of certain peculiar reactions for which no satisfactory explanation has been offered. Otto[2] found, for example, that unsymmetrical dihalogen derivatives of aliphatic hydrocarbons give symmetrical disulphones when heated with sulphinates.

$$CH_3CHBr_2 + 2RSO_2Na = \begin{matrix}CH_2SO_2R\\ |\\ CH_2SO_2R\end{matrix} + 2NaBr.$$

He explains this result by assuming a molecular rearrangement, an assumption for which there is no experimental evidence and which is improbable in view of the well-known stability of unsymmetrical disulphones. The discovery that sulphinic acids combine with unsaturated compounds suggests a different explanation, which does not involve molecular rearrangement.

[1] Ann. Chem. (Liebig), **306**, 53.
[2] J. prakt. Chem., [2], **40**, 505.

$$\text{I.}\quad \begin{matrix}CH_3\\|\\CHBr_2\end{matrix} + RSO_2Na = \begin{matrix}CH_3\\|\\CHBrSO_2Na\end{matrix} + NaBr;$$

$$\text{II.}\quad \begin{matrix}CH_3\\|\\CHBrSO_2Na\end{matrix} + RSO_2Na = \begin{matrix}CH_2\\||\\CHSO_2Na\end{matrix} + RSO_2H + NaBr;$$

$$\text{III.}\quad \left[\begin{matrix}CH_2\\||\\CHSO_2R\end{matrix}\right] + \begin{matrix}SO_2R\\|\\H\end{matrix} = \begin{matrix}CH_2SO_2R\\|\\CH_2SO_2R\end{matrix}.$$

We tried to isolate the hypothetical unsaturated sulphone (included in brackets) but failed. We obtained the halogen sulphone and found that when it is heated with a sulphinate most of the latter is transformed into the corresponding "disulphoxide." Since these disulphoxides are very easily obtained from sulphinic acids and not from sulphinates, this result indicates that at some stage of the process sulphinic acid is liberated as required by the above explanation.

I. Addition of Paratoluenesulphinic Acid to Aliphatic Aldehydes.

Paratoluenesulphinic acid dissolves in liquid aliphatic aldehydes with considerable evolution of heat. The addition-products which separate from this solution on cooling generally contain considerable quantities of unchanged sulphinic acid. They may be purified by repeated solution in ether and precipitation with ligroin, but pure products are more easily obtained by allowing the reaction to take place in ethereal solution. The method of procedure used in the preparation and purification of the substances described below, was as follows: A considerable excess of the aldehyde was added to an ethereal solution of the acid and the mixture boiled for half an hour. The liquid was then cooled in ice-water and ligroin added until precipitation just commenced. The crystalline precipitate which separated was redissolved in ether which contained a small quantity of the aldehyde and

again precipitated with ligroin. This process was repeated until the product was free from acid. Then the substance was dried rapidly in a current of air and analyzed at once.

1. Addition to Acetaldehyde: 1-Paratolylsulphonethanol(1), $CH_3CH\begin{matrix}OH\\SO_3C_7H_7\end{matrix}$.—The compound crystallizes in thick plates, which may be kept in ether and ligroin containing a small quantity of acetaldehyde. When dry, it loses aldehyde slowly in the cold, rapidly on heating. For this reason it does not melt sharply. It begins to soften at 52° and is liquid at 72°.

I. 0.2291 gram substance gave 0.4531 gram CO_2 and 0.1261 gram H_2O.

II. 0.2254 gram substance gave 0.4442 gram CO_2.

III. 0.2089 gram substance gave 0.2692 gram $BaSO_4$.

	Calculated for $C_9H_{12}SO_3$.	Found. I.	II.	III.
C	54.00	53.94	53.73	....
H	6.00	6.11	....	....
S	16.00	....	....	16.5

2. Addition to Isobutyric Aldehyde: 1-Paratolylsulphone-3-methylpropanol(1), $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH.CH\begin{matrix}OH\\SO_3C_7H_7\end{matrix}$.—The substance crystallizes from ether in colorless needles; from ether and ligroin in thick plates. It slowly decomposes in the air. An analysis gave the following result:

0.2020 gram substance gave 0.4277 gram CO_2 and 0.1290 gram H_2O.

	Calculated for $C_{11}H_{16}SO_3$.	Found.
C	57.90	57.67
H	7.02	7.09

3. Addition to Heptoic Aldehyde: 1-Paratolylsulphoneheptanol(1), $CH_3(CH_2)_4CH\begin{matrix}OH\\SO_3C_7H_7\end{matrix}$.—This product is less soluble in ether than the substances previously described, hence it was possible to purify it by dissolving it in boiling anhy-

drous ether and cooling the solution in ice-water. It crystallizes in fine, white needles, which decompose on heating. It is insoluble in water and ligroin; readily soluble in ether, alcohol, acetone, benzene, and chloroform. It loses aldehyde on exposure to the air.

I. 0.1932 gram substance gave 0.4361 gram CO_2 and 0.1386 gram H_2O.

II. 0.2224 gram substance gave 0.5020 gram CO_2 and 0.1608 gram H_2O.

	Calculated for $C_{14}H_{22}SO_3$.	Found. I.	II.
C	52.22	61.56	61.55
H	8.15	7.97	8.03

II. Addition of Paratoluenesulphinic Acid to Aromatic Aldehydes.

Paratoluenesulphinic acid combines with aromatic aldehydes under the same conditions as those under which it combines with aliphatic aldehydes. The compound with benzaldehyde was not obtained in pure condition. The compounds with metanitrobenzaldehyde and paranitrobenzaldehyde, however, are much more stable than the corresponding compounds with aliphatic aldehydes. They do not change in the air, and they can be recrystallized from alcohol, acetone, and other organic solvents.

1. Addition to Metanitrobenzaldehyde: 1-Paratolylsulphone-1-metanitrophenylmethanol, $m\text{-}NO_2C_6H_4CH\langle^{OH}_{SO_2C_7H_7}$.—Ethereal solutions of the aldehyde and the acid were mixed and warmed on the water-bath. After a few minutes the product separated in fine, white needles, that melt to a yellow liquid at 110°.

0.2860 gram substance gave 0.5738 gram CO_2 and 0.1139 gram H_2O.

	Calculated for $C_{14}H_{13}NSO_4$.	Found.
C	54.72	54.71
H	4.23	4.43

The substance is readily soluble in alcohol and acetone, slightly soluble in ether. It is decomposed by boiling water, which dissolves the acid and leaves most of the aldehyde. A solution of sodium carbonate decomposes it slowly in the cold.

2. Addition to Paranitrobenzaldehyde: 1-Paratolylsulphone-1-paranitromethanol, $p\text{-}NO_2C_6H_4CH\langle^{OH}_{SO_2C_7H_7}$. – The addition was carried out in ethereal solution and the product recrystallized from acetone.

0.2028 gram substance gave 0.4070 gram CO_2 and 0.0786 gram H_2O.

	Calculated for $C_{14}H_{13}NSO_5$.	Found.
C	54.72	54.73
H	4.23	4.08

The substance crystallizes in pale-yellow needles, melting at 116°. It is soluble in alcohol and acetone, slightly soluble in ether, insoluble in ligroin and water.

While this work was in progress Meyer[1] described a substance which he obtained by the direct union of paratoluenesulphinic acid and formaldehyde. By treating this substance —paratolylsulphonecarbinol—with acetic anhydride, Meyer obtained an acetyl derivative, and by treating it with aniline he obtained an anilide. Since the product obtained from paranitrobenzaldehyde is more stable than the corresponding aliphatic compounds, we expected it to give similar products with these reagents. This is not the case. The substance dissolves completely in cold acetic anhydride, and when this solution is allowed to evaporate the acetal of paranitrobenzaldehyde separates in beautiful, needle-shaped crystals that melt at 126°.5.

0.1977 gram substance gave 0.8771 gram CO_2 and 0.0784 gram H_2O.

	Calculated for $NO_2C_6H_4CH\langle^{OCOCH_3}_{OCOCH_3}$.	Found.
C	52.17	52.01
H	4.35	4.40

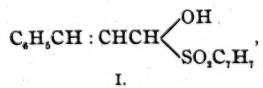
[1] J. prakt. Chem., [2], 63, 167.

The acetal is formed from the oxysulphone much more easily than from the aldehyde itself, since no acetal was obtained when a solution of the aldehyde in acetic anhydride was boiled with an inverted condenser or heated in a sealed tube to 150°. A fair yield of the acetal was obtained, however, by boiling a solution of the aldehyde in acetic anhydride, to which a small quantity of concentrated sulphuric acid had been added.

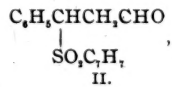
To test the action of aniline on the oxysulphone a small quantity of the substance was added to a boiling solution of aniline in ether. The substance dissolved and fine, white needles separated from the hot solution. These were very soluble in water and alcohol, insoluble in ether. They melted at 121° to 122°. Since the same substance was obtained by treating paratoluenesulphinic acid with aniline in ethereal solution, it must be the aniline salt of paratoluenesulphinic acid. This shows that the oxysulphone is easily decomposed by aniline.

III. Addition of Paratoluenesulphinic Acid to Cinnamic Aldehyde.

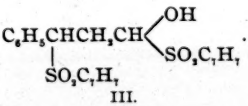
Cinnamic aldehyde combines with acid sulphites to form three different substances. The corresponding addition-products with paratoluenesulphinic acid would be represented by the following formulas:



I.



II.



III.

Only two of these substances were obtained; the monosulphone represented by II. and the disulphone represented by III. Whether the monosulphone or disulphone be formed in any given experiment depends partly upon the conditions and

partly upon the relative amounts of the substances. When the acid is dissolved in the aldehyde, and when the two are brought together in ethereal solution, the product is the disulphone, even when the aldehyde is present in large excess. This result is due to the difference in the solubility of the monosulphone and the disulphone in these media. In water and in alcohol, where there is no such difference, the result depends upon the relative amounts of acid and aldehyde that are brought together.

The *monosulphone* crystallizes in white, globular aggregates that melt at 78°. It is readily soluble in alcohol, ether, and benzene, insoluble in water and ligroin. An analysis gave the following results:

0.2285 gram substance gave 0.5580 gram CO_2 and 0.1101 gram H_2O.

	Calculated for $C_{16}H_{16}SO_3$.	Found.
C	66.66	66.59
H	5.55	5.35

That the substance has the structure (II.) assigned to it is shown by the following experiments:

1. An ethereal solution of the substance was shaken with an aqueous solution of acid potassium sulphite. A crystalline compound separated at once. When this was treated with dilute alkalies the original substance was regenerated. This result proves the presence of the aldehyde group.

2. The substance was oxidized by warming it with dilute nitric acid (1 : 3) on the water-bath. An acid separated from the solution, on cooling, in fine, white needles, melting at 196° to 197°. This same acid was obtained by adding paratoluenesulphinic acid to cinnamic acid, and it will be shown below that its structure is represented by the formula

$$C_6H_5CHCH_2CO_2H$$
$$|$$
$$SO_2C_7H_7$$

This proves that the sulphone group is in the β-position with reference to the aldehyde group.

The disulphone (III.) is obtained by treating either the

aldehyde or the monosulphone with paratoluenesulphinic acid in ethereal solution. It is soluble in benzene, alcohol, and water. From the last it separates in fluffy white needles which melt, with decomposition, at about 126°. The analyses gave no concordant results, since it is not possible to recrystallize it without partial decomposition into the monosulphone and the sulphinic acid. It was found, however, that in ethereal solution 1 molecule of cinnamic aldehyde combines with exactly 2 molecules of paratoluenesulphinic acid.

IV. Addition of Sulphinic Acids to 1,2-Unsaturated Acids.

2. Addition of Paratoluenesulphinic Acid to Cinnamic Acid: β-Paratolylsulphonehydrocinnamic Acid, $C_6H_5CHCH_2CO_2H$.—
$C_7H_7SO_2$

Equivalent quantities of paratoluenesulphinic acid and cinnamic acid were boiled in water, in a flask connected with an inverted condenser. Both acids melted to an oil under water. This oil gradually solidified, and after boiling for three days none was left. The solid was then filtered off and treated with a hot solution of sodium carbonate, in which nearly all of it dissolved. The part that was insoluble in the solution of sodium carbonate was repeatedly crystallized from alcohol and thus separated into paratolyldisulphoxide and distyrene. Since the former is always formed when the sulphinic acid is heated with water, and the latter when solutions of cinnamic acid are boiled, these substances are not connected with the principal reaction.

On cooling the hot solution in sodium carbonate a sodium salt separated as a heavy, white precipitate. This was dried on a porcelain plate, the dry salt extracted with boiling ether, and the residue dissolved in water. From this solution dilute sulphuric acid precipitated an acid which was recrystallized from large quantities of boiling water and analyzed.

0.1608 gram substance gave 0.3719 gram CO_2 and 0.0725 gram H_2O.

	Calculatrd for $C_{16}H_{16}SO_4$.	Found.
C	63.15	63.08
H	5.26	5.02

The acid was evidently formed by the direct union of 1 molecule of cinnamic acid and 1 molecule of the sulphinic acid. To locate the sulphone group the following method was used. Fittig found that hydrobromic acid combines with cinnamic acid to form β-bromhydrocinnamic acid. This acid, when treated with sodium toluenesulphinate, should give a β-sulphonehydrocinnamic acid which could be compared with the acid obtained by addition. We found, however, that the bromo-acid is decomposed by the sulphinate in the same way n which it is decomposed by carbonates:

$$C_6H_5CHBrCH_2CO_2H + RSO_2Na = C_6H_5CH{=}CH_2 + C_7H_7SO_2H + NaBr + CO_2.$$

To guard against this decomposition we tried the methyl ester in place of the acid itself.

Cinnamic acid was dissolved in absolute methyl alcohol and the solution saturated with hydrobromic acid. The methyl ester of β-bromhydrocinnamic acid crystallized out on standing. Equivalent quantities of this methyl ester and the sodium salt of paratoluenesulphinic acid were dissolved in methyl alcohol and the solution boiled until there was no further separation of sodium bromide. The liquid was filtered, the filtrate evaporated to dryness, and the residue recrystallized from ether. The pure ester obtained in this way was saponified by boiling it with dilute hydrochloric acid until everything had gone into solution. The acid which crystallized on cooling this solution was the same as that which had been obtained by addition; the latter, therefore, has the sulphone group in the β-position with reference to carboxyl. A better way to prepare the substance is to heat the mixture of cinnamic and sulphinic acids with water in sealed tubes to 110°. The solid that separates contains a much smaller amount of by-product.

β-Paratolylsulphonehydrocinnamic acid is almost insoluble in cold water; it dissolves slowly in boiling water, from which it separates, on cooling, in fine needles. It is readily soluble in alcohol and ether, very slightly soluble in ligroin. It is most easily purified through the sodium salt. It melts at 197° to 198° without decomposition.

The *sodium salt* was prepared by dissolving the acid in a hot solution of sodium carbonate, from which the salt separated on cooling. It was dried and crystallized from boiling alcohol. The analyses show that it contains 2 molecules of water of crystallization, only one of which can be driven off without decomposing the salt:

I. 0.1301 gram salt gave 0.0254 gram Na_2SO_4.
II. 0.0877 gram salt gave 0.0172 gram Na_2SO_4.
III. 0.2174 gram salt gave 0.0117 gram H_2O at 130°.
IV. 0.2057 gram dried salt gave 0.0437 gram Na_2SO_4.

	Calculated for $C_{18}H_{16}O_4SNa_2.2H_2O$.	Found. I.	II.	III.
Na	6.35	6.32	6.35	....
H_2O (1 mol.)	5.00	....	....	5.30

	Calculated for $C_{18}H_{15}O_4ONa.H_2O$.	Found.
Na	6.68	6.88

The salt crystallizes from alcohol in fine, white needles. It has an exceedingly bitter taste.

The *calcium salt*, made by boiling the acid with calcium carbonate suspended in water, crystallizes in plates. It is moderately soluble in water.

I. 0.1683 gram salt gave 0.0330 gram $CaSO_4$.
II. 0.1198 gram salt gave 0.0239 gram $CaSO_4$.

	Calculated for $(C_{18}H_{18}O_4S)_2Ca$.	Found. I.	II.
Ca	6.18	5.73	5.85

The *barium salt*, made like the calcium salt, crystallizes with 4 molecules of water of crystallization.

I. 0.1258 gram substance gave 0.0356 gram $BaSO_4$.
II. 0.0770 gram substance gave 0.0216 gram $BaSO_4$.
III. 0.1220 gram substance lost 0.0110 gram at 15°.

	Calculated for $(C_{18}H_{15}SO_4)_2Ba$.	Found. I.	II.	III.
Ba	16.78	16.62	16.49	....
$4H_2O$	8.83	....	....	9.00

The *methyl ester* was made by boiling the acid with a 3 per cent solution of hydrochloric acid in methyl alcohol. It crystallizes from methyl alcohol in fine, white needles, which melt at 156°.

0.1989 gram substance gave 0.4660 gram CO_2 and 0.1010 gram H_2O.

	Calculated for $C_{17}H_{18}SO_4$.	Found.
C	64.15	63.89
H	5.63	5.64

The ester is not decomposed by boiling with water. Boiling hydrochloric acid saponifies it, and boiling caustic potash decomposes it into the potassium salt of paratoluenesulphinic acid and methyl cinnamate.

2. Addition of Benzenesulphinic Acid to Cinnamic Acid: β-Phenylsulphonehydrocinnamic Acid, $C_6H_5CH(SO_2C_6H_5)CH_2CO_2H$.—A mixture of the two acids was suspended in water and the liquid boiled for several days. The product was purified by recrystallization from boiling water, from which it separated in shining plates melting at 173°.

0.2542 gram substance gave 0.5770 gram CO_2 and 0.1123 gram H_2O.

	Calculated for $C_{15}H_{14}SO_4$.	Found.
C	62.00	61.80
H	4.83	4.84

The acid is readily soluble in alcohol and ether; very slightly in ligroin.

The *barium salt* crystallizes in needles, moderately soluble in water, insoluble in alcohol.

0.0993 gram salt gave 0.0310 gram $BaSO_4$.

	Calculated for $(C_{15}H_{13}SO_4)_2Ba$.	Found.
Ba	18.60	18.40

The *ethyl ester* was made by saturating with hydrochloric acid a solution of the acid in absolute alcohol. It crystallizes from alcohol in small, white needles melting at 139°.

I. 0.1486 gram substance gave 0.3490 gram CO_2 and 0.0764 gram H_2O.

II. 0.1314 gram substance gave 0.3078 gram CO_2 and 0.0670 gram H_2O.

	Calculated for $C_{17}H_{18}SO_4$.	Found. I.	Found. II.
C	64.15	64.05	63.89
H	5.63	5.54	5.66

The ester is not changed by protracted boiling with water. When boiled with dilute hydrochloric acid it is saponified to the corresponding acid. When boiled with a dilute solution of caustic potash it is decomposed into cinnamic and benzenesulphinic acids.

3. Addition of Paratoluenesulphinic Acid to Fumaric and Maleic Acids: β-Paratolylsulphonepropionic Acid, $C_7H_7SO_2CH_2CH_2CO_2H$.—An aqueous solution containing paratoluenesulphinic acid and fumaric acid in molecular proportions was boiled until the oil that separated at first had completely solidified. The product was dissolved in a solution of sodium carbonate, the solution extracted with ether, and the acid reprecipitated with dilute sulphuric acid. After crystallization from hot water it gave the following results on analysis:

0.1819 gram substance gave 0.3536 gram CO_2 and 0.0990 gram H_2O.

	Calculated for $C_{10}H_{12}SO_4$.	Found.
C	52.58	53.01
H	5.31	6.03

These results indicated that the substance was not an addition-product, but a monobasic acid formed from the addition-product by loss of carbon dioxide:

$$\begin{matrix} CHCO_2H \\ \| \\ CHCO_2H \end{matrix} + \begin{matrix} SO_2C_7H_7 \\ H \end{matrix} =$$

$$\begin{matrix} & & SO_2C_7H_7 \\ & CH & \diagup \\ & \vert & \diagdown CO_2H \\ CH_2CO_2H & \vert & \end{matrix} \longrightarrow C_7H_7SO_2CH_2CH_2CO_2H + CO_2.$$

Since repeated recrystallizations failed to give an acid that had a sharp melting-point or that gave concordant results on analysis, maleic acid was substituted for fumaric acid in the

hope that the latter would give the same product without requiring the prolonged boiling necessary with the former. It was found that maleic acid, as expected, gave the same product as fumaric acid, but the substance was just as impure and just as difficult to purify as that obtained from fumaric acid. It melted from 107° to 115°.

The same acid was, however, obtained in a pure condition by treating β-iodopropionic acid with the sodium salt of paratoluenesulphinic acid. Fifty grams of β-iodopropionic acid were exactly neutralized with a solution of sodium carbonate, the calculated amount of the sulphinate was added to this solution, and the whole evaporated to dryness on the water-bath. The dark, reddish-brown residue was dissolved in dilute hydrochloric acid and the solution decolorized with bone-black. On evaporating the solution slowly the acid separated in needles melting at 110° to 113°.

I. 0.2237 gram substance gave 0.4280 gram CO_2 and 0.1076 gram H_2O.

II. 0.1167 gram substance gave 0.2248 gram CO_2 and 0.0589 gram H_2O.

	Calculated for $C_{10}H_{12}SO_4$.	Found. I.	II.
C	52.58	52.18	52.53
H	5.31	5.34	5.51

The acid was found identical with that obtained from fumaric acid and maleic acid. It is partially decomposed by repeated crystallizations from boiling water, the melting-point becoming considerably lower. This explains the difficulty in getting a pure product.

4. Addition of Paratoluenesulphinic Acid to Citraconic Acid:

Paratolylsulphonepyrotartaric Acid, $CH_3C(SO_2C_7H_7)(CO_2H)CH_2CO_2H$. — Ten grams of citraconic acid and 13.5 grams of paratoluenesulphinic acid were heated with water for two days at 110°. The liquid was then exactly neutralized with sodium carbonate, the solution extracted with ether, and evaporated to dryness.

The residue was dissolved in as small a quantity as possible of 50 per cent alcohol and this solution poured into an equal volume of absolute alcohol. The sodium salt precipitated at once. It was recrystallized by the same method. It separated in fine, white needles, containing 2 molecules of water of crystallization.

I. 0.2377 gram substance gave 0.0936 gram Na_2SO_4.
II. 0.2140 gram substance gave 0.0833 gram Na_2SO_4.
III. 0.3277 gram substance lost 0.0326 gram at 150°.

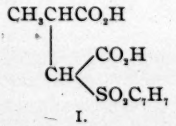
	Calculated for $C_{11}H_{18}SO_8Na_2.2H_2O$.	Found. I.	II.	III.
Na	12.60	12.65	12.65	....
$2H_2O$	9.84	....	....	9.97

On acidifying the aqueous solution of the sodium salt the acid separated as an oil. This was taken up with ether, and ligroin added slowly until the solution became slightly cloudy. On addition of a drop of ether the solution cleared up and the acid separated in small, lustrous prisms.

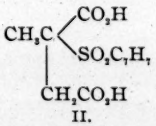
0.4118 gram substance gave 0.2226 gram CO_2 and 0.0979 gram H_2O.

	Calculated for $C_{12}H_{14}SO_6$.	Found.
C	50.35	50.45
H	4.89	4.88

The acid is extremely soluble in alcohol, ether, and acetone. It is insoluble in ligroin and chloroform. If precipitated from its solution in sodium carbonate it separates as an oil which does not solidify. It melts at 169° to 171°, and begins to lose carbon dioxide as soon as melted. An attempt to determine the structure of the acid by driving off carbon dioxide and identifying the residue failed because the acid broke down completely. The two possible formulas for the acid are :



I.



II.

Formula I. represents a mode of linkage which is known to be exceedingly unstable. The following equations illustrate a number of cases in which such a substance would be expected but where a decomposition-product is invariably obtained:

$$\begin{array}{l}\mathrm{CHBrCO_2H}\\ |\\ \mathrm{CH_2CO_2H}\end{array} + \mathrm{C_6H_5SO_2Na} = \begin{array}{l}\mathrm{CH_2SO_2C_6H_5}\\ |\\ \mathrm{CH_2CO_2H}\end{array} + \mathrm{NaBr} + \mathrm{CO_2};$$

$$\begin{array}{l}\mathrm{CHBrCO_2H}\\ |\\ \mathrm{CHBrCO_2H}\end{array} + 2\mathrm{C_6H_5SO_2Na} = \begin{array}{l}\mathrm{CH_2SO_2C_6H_5}\\ |\\ \mathrm{CH_2SO_2C_6H_5}\end{array} + 2\mathrm{NaBr} + 2\mathrm{CO_2};$$

$$\begin{array}{l}\mathrm{CHCO_2H}\\ \|\\ \mathrm{CHCO_2H}\end{array} + \mathrm{C_7H_7SO_2H} = \begin{array}{l}\mathrm{CH_2SO_2C_7H_7}\\ |\\ \mathrm{CH_2CO_2H}\end{array} + \mathrm{CO_2}.$$

As the acid in question is stable in solution and does not lose carbon dioxide below its melting-point, there can be little doubt that its structure is represented by II.

V. Addition of Paratoluenesulphinic Acid to Unsaturated Ketones.

Paratoluenesulphinic acid combines with unsaturated ketones with most surprising ease. When the acid and an unsaturated ketone are brought together in any organic medium the liquid almost immediately becomes warm, and in a very short time the sparingly soluble sulphoneketone crystallizes out in characteristic long, fine needles, which fill the entire liquid.

1. Addition of Paratoluenesulphinic Acid to Benzalacetone, $\begin{array}{l}\mathrm{C_6H_5CHCH_2COCH_3}\\ |\\ \mathrm{SO_2C_7H_7}\end{array}$. — The sulphoneketone was made by bringing the components together in alcoholic solution and recrystallizing the product from alcohol.

0.2322 gram substance gave 0.5737 gram CO_2 and 0.1251 gram H_2O.

	Calculated for $C_{17}H_{18}SO_3$.	Found.
C	67.54	67.38
H	5.96	5.98

The compound is readily soluble in acetone; moderately soluble in boiling alcohol and boiling benzene; insoluble in water. It separates from hot alcohol in fine, white needles, which pass into a more compact form when allowed to remain in contact with the cold solution.

The sulphoneketone slowly dissolves in a warm solution of bleaching powder, which breaks it down into chloroform and β-paratolylsulphonehydrocinnamic acid:

$$\begin{array}{l} C_6H_5CHCH_2COCH_3 \\ \quad\quad | \\ \quad SO_2C_7H_7 \end{array} + 6Cl + H_2O = \begin{array}{l} C_6H_5CHCH_2CO_2H \\ \quad\quad | \\ \quad SO_2C_7H_7 \end{array} + 3HCl + CHCl_3.$$

The chloroform is obtained by distillation; the acid crystallizes out on acidifying the cold solution. This result shows that the sulphone group is in the β-position with reference to the carbonyl group.

The sulphoneketone can be boiled with dilute acids without appreciable change, but dilute alkalies rapidly decompose it. Thus, when a small quantity of the ketone was suspended in a solution of potassium hydroxide and the liquid distilled, a mixture of benzalacetone and its decomposition-products, benzaldehyde and acetone, passed off with the steam while the potassium salt of paratoluenesulphinic acid went into solution. A similar change takes place when the substance is treated with phenylhydrazine.

Two grams of the compound and 0.7 gram of phenylhydrazine were dissolved in alcohol and the solution boiled for several hours. On partly evaporating the solution two kinds of crystals separated: some very soluble in cold ether, and smaller crystals soluble only in boiling ether. The mixture was separated by repeated extraction with cold ether.

The ethereal solution was mixed with a little alcohol and the mixture evaporated until all the ether had been driven

off. Water was then added until the solution became cloudy. On cooling this solution, a substance separated in long needles of a bright lemon-yellow color. The melting-point (159°) indicated the phenylhydrazone of benzalacetone, and this was confirmed by comparing the substance with a preparation made directly from the ketone.

The crystals which were not dissolved by the cold ether were recrystallized from boiling ether and analyzed.

0.1126 gram substance gave 0.2450 gram CO_2 and 0.0563 gram H_2O.

	Calculated for $C_7H_7SO_2H.C_6H_5NH.NH_2$.	Found.
C	59.08	59.32
H	6.06	5.55

That the substance is the phenylhydrazine salt of para-toluenesulphinic acid was established by comparing it with a specimen made directly from the acid. The salt crystallizes in needles. It melts with decomposition at 160° to 165°.

The mother-liquor, from which the hydrazone and the salt just described had separated, deposited a third substance on slow evaporation. After purification from alcohol this was obtained in long, branching, straw-colored crystals, which melted without change at 114°. An analysis gave the following results:

0.2031 gram substance gave 0.6047 gram CO_2 and 0.1251 gram H_2O.

	Calculated for $C_{18}H_{18}N_2$.	Found.
C	81.35	81.19
H	6.78	6.84

The compound gives a deep blue color with nitrous acid, and the characteristic reddish-purple color of the pyrazol derivatives when treated with ferric chloride in acid solution. It is 1,5-diphenyl-3-methylpyrazoline. The action of phenylhydrazine on the sulphoneketone is represented by the following equations:

I. $$\begin{matrix} C_6H_5CHCH_2COCH_3 \\ | \\ SO_2C_7H_7 \end{matrix} + 2C_6H_5NH.NH_2 = \begin{matrix} C_6H_5CH{=}CHCCH_3 \\ \quad\quad\quad\

sodium salt this was found to be β-paratolylsulphonehydrocinnamic acid, showing that in the sulphoneketone the sulphone group is in the β-position. Many attempts were made to add a second molecule of sulphinic acid to the sulphoneketone or to add 2 molecules of the sulphinic acid to the unsaturated ketone, but all of them failed. This is remarkable, since the monosulphone readily combines with 2 atoms of bromine. Eight-tenths of a gram of bromine were added to 2 grams of the sulphone dissolved in chloroform and the liquid set aside until the color of bromine had disappeared. The chloroform was then evaporated and the residue recrystallized from alcohol. A bromine determination gave the following result:

0.1557 gram substance gave 0.1058 gram AgBr.

	Calculated for $C_{24}H_{22}SBr_2O_3$.	Found.
Br	29.09	28.85

The bromine addition-product crystallizes from alcohol in needles closely resembling the original substance. It is very soluble in chloroform; moderately soluble in alcohol; insoluble in ether, acetone, and glacial acetic acid.

3. Addition of Paratoluenesulphinic Acid to Benzalacetophenone.—One gram of the sulphinic acid was added to a solution of 1 gram of benzalacetophenone in alcohol. A white, crystalline solid separated at once. It was recrystallized from alcohol and analyzed.

0.2574 gram substance gave 0.6826 gram CO_2 and 0.1186 gram H_2O.

	Calculated for $C_{23}H_{20}SO_3$.	Found.
C	72.52	72.32
H	5.49	5.12

The substance crystallizes in needles melting at 169° to 170°.

4. Addition of Paratoluenesulphinic Acid to Cinnamylideneacetone, $C_6H_5CH:CH.\underset{\displaystyle SO_2C_7H_7}{\underset{|}{C}}HCH_2COCH_3$.—Cinnamylideneacetone

contains the combination of single and double linkages which Thiele[1] has called "a conjugated system of vicinal double unions." When it combines with 1 molecule of a sulphinic acid, the sulphone group ought, according to Thiele's theory, to go into the δ-position. The following results show that this is not the case; the sulphone group goes into the β-position.

Equivalent quantities of cinnamylideneacetone and paratoluenesulphinic acid were dissolved in cold acetone. The addition-product began to separate in a few minutes, and the reaction was complete in less than half an hour. The product, after crystallization from alcohol, melted at 125° to 126°. An analysis gave the following results:

0.2036 gram substance gave 0.5175 gram CO_2 and 0.1122 gram H_2O.

	Calculated for $C_{19}H_{20}SO_3$.	Found.
C	69.50	69.33
H	6.09	6.12

When the finely powdered sulphoneketone was warmed with a concentrated solution of bleaching-powder it gave a number of different substances, some of which dissolved while others remained suspended in the liquid. The insoluble substances were filtered off and discarded. The excess of bleaching-powder in the solution was reduced with acid potassium sulphite, the solution acidified with dilute hydrochloric acid, and repeatedly extracted with ether. The ether, on evaporation, left an oily residue containing benzoic acid, an unsaturated acid, and one or more acids containing halogen. The oil was suspended in water and distilled in a current of steam. Pure benzoic acid was carried into the distillate. The residue from the benzoic acid was dissolved in ether and the dry ethereal solution allowed to evaporate slowly. Only oils separated and all efforts to get solid substances from the oils failed. The entire residue was therefore dissolved in potassium hydroxide and carefully treated with potassium permanganate until the purple color of the permanganate no longer disappeared in the cold. The excess of permanganate

[1] Ann. Chem. (Liebig), **306**, 53.

and the oxides of manganese were then reduced with acid potassium sulphite and the solution made strongly acid with sulphuric acid. The oxidation-product crystallized out in long, brittle needles melting at 113°. Analyses, melting-point, and properties showed that the substance is β-paratolylsulphonepropionic acid. This result proves that when the sulphinic acid combines with the ketone the sulphone group goes into the β-position. The successive steps are shown by the following equations:

I. $$C_6H_5CH:CH.CHCH_2COCH_3 + 6Cl + H_2O = \begin{matrix} C_6H_5CH:CHCHCH_2CO_2H \\ | \\ SO_2C_7H_7 \end{matrix} + CHCl_3;$$

II. $$C_6H_5CH:CH.CHCH_2CO_2H + 4O = \begin{matrix} C_6H_5CO_2H + HO_2CCHCH_2CO_2H \\ | \\ SO_2C_7H_7 \end{matrix};$$

III. $$HO_2CCHCH_2CO_2H = C_7H_7SO_2CH_2CH_2CO_2H + CO_2.$$

$SO_2C_7H_7$

6. Addition of Paratoluenesulphinic Acid to Cinnamylideneacetophenone, $C_6H_5CH:CH.CHCH_2COC_6H_5$.—The substances combine in the cold. The product crystallizes from acetone in needles that melt at 145°. An analysis gave the following results:

0.1860 gram substance gave 0.5023 gram CO_2 and 0.0972 gram H_2O.

	Calculated for $C_{24}H_{22}O_3S$.	Found.
C	73.84	73.61
H	5.64	5.80

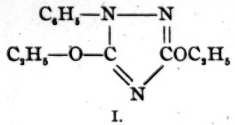
We expect to continue this work with acids that contain conjugated systems of double unions.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
November, 1903.

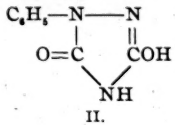
A NOTE ON SOME OF THE REACTIONS IN THE URAZOLE SERIES.

By S. F. Acree.

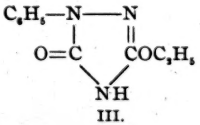
In a recent number of this JOURNAL[1] appeared an article by Wheeler and Johnson in which were described some experiments in the urazole series, the results of which depart widely from those obtained by the present writer. Wheeler and Johnson state that by the action of ethyl iodide on monosilver phenylurazole they were able to obtain 1-phenyl-3,5-diethoxyurazole[2] (I.) and phenylurazole (II.), but no 1-phenyl-3-ethoxyurazole (III.), which is indeed the chief product of the reaction. This 1-phenyl-3-ethoxyurazole (III.) was formerly[3] in hand in slightly impure state, and directions have been recently published[4] for obtaining it in a pure state by this very reaction.



I.



II.



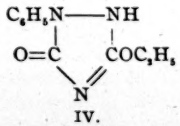
III.

The cause of Wheeler and Johnson's failure to obtain the 1-phenyl-3-ethoxyurazole (III.) found by this reaction is at once clear from their article. This ethoxy derivative is the normal reaction-product, and they should have done their experimental work with the main object of securing this substance. From their article, one could suspect that they entirely overlooked the fact that such a substance could be formed. Although they say (p. 32) "It seemed incredible

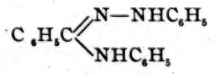
[1] Wheeler and Johnson: This JOURNAL, 30, 24 (1903).
[2] Wheeler and Johnson: *Loc. cit.*; Acree: Ber. d. chem. Ges., 36, 3148.
[3] Acree: This JOURNAL, 27, 131; Ber. d. chem. Ges., 35, 559.
[4] Acree: Ber. d. chem. Ges., 36, 3146.

that a monoethyl derivative of phenylurazole should be insoluble in alkali," yet they dissolve this ethoxy derivative in alkali and discard this alkaline solution. They extracted an ethereal solution containing 1-phenyl-3,5-diethoxyurazole (insoluble in alkalies) and 1-phenyl-3-ethoxyurazole (soluble in alkalies) with an alkaline solution (p. 39), thereby removing the 1-phenyl-3-ethoxyurazole from the ethereal solution. They then examined the ethereal solution and found the 1-phenyl-3,5-diethoxyurazole (which melts at 53° instead of at 46° to 47°, as stated by Wheeler and Johnson). They evidently entirely forgot to examine the alkaline extraction-solution and thus failed to find the 1-phenyl-3-ethoxyurazole. If Wheeler and Johnson will repeat their work, using the suggestions above offered, the writer is sure that they will have no difficulty in obtaining the 1-phenyl-3-ethoxyurazole formed in this reaction.

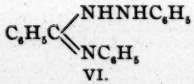
Wheeler and Johnson take exceptions to Acree's supposition that the substance 1-phenyl-2-hydro-3-ethoxyurazole (IV.) might exist as a definite compound, tautomeric with 1-phenyl-3-ethoxy-4-hydrourazole (III.). These writers believe that these two formulas probably represent the same substance. The possibility of this kind of tautomerism is proved beyond question by the isolation of just such tautomeric benzenyldiphenylhydrazidines[1] (V. and VI.) and the tautomeric methenylphenyltoluylamidines[2] (VII. and VIII.).



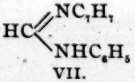
IV.



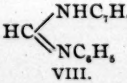
V.



VI.



VII.

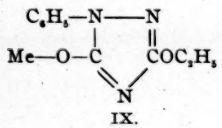


VIII.

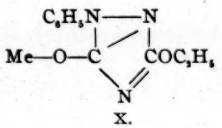
That the form IV. can possibly rearrange into the form III., or *vice versa*, can hardly be doubted. Indeed it might very

[1] v. Pechmann: Ber. d. chem. Ges., 28, 869, 2362.
[2] Walther: J. prakt. Chem., 55, 41.

well be that the form IV. rearranges into the form III. under all conditions which we can easily realize, and that we cannot obtain it as a distinct substance, or can obtain it only with great difficulty. Although the substance has not yet been made, and predictions are unsafe, the present writer believes that this substance, as such, will not exhibit the acid properties possessed by the other known monoalkylphenylurazoles. If it forms stable neutral (in water) alkali salts, it will be because it undergoes rearrangement and forms salts somewhat like IX or X.



IX.



X.

This does not mean that the writer believes it to be impossible to obtain the isomeric salts,

$$-NMe-C=O \quad \text{and} \quad -N=C-O-Me,$$

of these urazoles and other amides. Indeed, this very hypothesis was put forward over two years ago in the following words[1] to account for the properties of disodium phenylurazole: "Although the disodium salt can be formed by boiling phenylurazole with sodium alcoholate, in absolute alcohol, yet it gives a strongly alkaline reaction, when dissolved in water, indicating that one of the sodium atoms of the salt is joined to a nitrogen atom of the urazole ring."

Since then, Lander[2] has used a similar hypothesis to explain the reactions between alkyl haloids and the salts of tautomeric compounds. Hantzsch[3] has isolated two different mercury salts of cyanuric acid, and Titherly[4] has noticed similar phenomena in the silver salts of benzamide and acetamide.

Wheeler and Johnson state that by the action of a molecu-

[1] Acree: This JOURNAL, 27, 119.
[2] Lander: J. Chem. Soc. (London), 83, 414 (1903).
[3] Hantzsch: Ber. d. chem. Ges., 35, 2717 (1902).
[4] Titherly: J. Chem. Soc. (London), 79, 409 (1901).

lar proportion of acetyl chloride on monosilver phenylurazole[1] they obtained a new diacetyl derivative of phenylurazole, but no monoacetyl derivative. A monoacetyl derivative should be, of course, the normal reaction-product. As published before,[2] the chief product of this reaction is monoacetylphenylurazole, which melts at 173°. This experiment has been repeated several times under widely varying conditions. Various samples of the monoacetyl derivative so obtained have been analyzed, and have been converted into 1-phenyl-4-methylacetylurazole by means of diazomethane. The writer has used very pure silver phenylurazole in these experiments. As Wheeler and Johnson state that their silver phenylurazole contained 39 per cent silver instead of 37.9 per cent, the writer believes that their results differ from ours on account of the impurities (possibly some disilver phenylurazole) in their silver salt.

Small quantities of diacetylphenylurazole and of phenylurazole are generally obtained as by-products. This is entirely analogous to the formation of 1-phenyl-3,5-diethoxyurazole and phenylurazole as by-products in the reaction between silver phenylurazole and ethyl iodide, 1-phenyl-3-ethoxyurazole being the chief product of the reaction. The formation of these small quantities of by-products has been explained in a previous paper.[3]

The writer can only suggest that if Wheeler and Johnson will repeat their work, using pure silver phenylurazole, they will obtain the same results that the present writer has above described.

UNIV. OF BERLIN, Nov. 1, 1903.

REVIEWS.

AUSGEWÄHLTE METHODEN DER ANALYTISCHEN CHEMIE. Von PROF. DR. A. CLASSEN. Zweiter Band. Braunschweig: Friedrich Vieweg und Sohn. 1903. pp. xvi + 831.

The first volume of this work was reviewed in this JOURNAL for May, 1901 (Vol. XXV., p. 437). It was devoted mainly

[1] Wheeler and Johnson: This JOURNAL, 30, 37.
[2] Acree: Ber. d. chem. Ges., 36, 3143 (foot-note).
[3] Acree: *Ibid.*, 36, 3147.

to processes for the detection and determination of the metallic elements and their compounds. The second volume covers like ground for the non-metals. The field is for the most part restricted to compounds usually spoken of as inorganic, though methane, ethylene, and acetylene are included, as also the cyanides and compound cyanides, and the methods of ultimate or elementary organic analysis. Notice is taken of sundry substances of which our knowledge has been acquired within recent years, as for example, the long unobserved atmospheric gases—helium, neon, argon, krypton, and xenon (the characteristic spectra of which are shown in a well-printed table in colors),—the percarbonates, persulphates, and carborundum.

The larger part of the matter is drawn from German sources, although methods originating elsewhere than in Germany are not altogether neglected. Thus attention is given to some of the processes suggested by Hillebrand and Gooch in this country.

In regard to the degree of fulness with which methods of technical interest are treated there seems to be some inequality. The examination of ordinary potable water and of mineral waters takes up 117 pages, while but 15 pages are given to the important subject of explosives. No attempt appears to have been made to supplement matters treated of in the first volume by adding the results of more recent researches. For example, there is no account of the lately developed improvements in methods for the detection of minute quantities of arsenic in beer and other complex organic mixtures.

On the whole, however, the new volume contains much useful and valuable information, and, like its precursor, is handsomely printed and illustrated. J. W. M.

GRUNDRISS DER REINEN UND ANGEWANDTEN ELEKTROCHEMIE. Von P. FERCHLAND, Dr. Phil. Mit 59 Figuren im Text. Halle a. S. Verlag von Wilhelm Knapp. pp. 271. 1903.

The book in hand is an elementary treatise on electrochemistry. The scope of the work is not widely different from that of several books in this field. The more important chapters deal with: The Law of Faraday, Transference Numbers, Conductivity, Theories of Electrolysis, The Theory of Electrolytic Dissociation, Calculation and Measurement of Electromotive Force, The New Theory of Electrolysis, Absolute Differences in Potential and Polarization.

The book is clearly and judiciously written, and will doubtless find its place in the literature of electrochemistry.

H. C. J.

A TEXT-BOOK OF ORGANIC CHEMISTRY. By DR. A. F. HOLLEMAN, Professor Ordinarius in the University of Groningen, Netherlands. Translated from the second Dutch Edition by A. JAMIESON WALKER, PH.D. (Heidelberg), B. A., Head of the Department of Chemistry, Municipal Technical College, Derby, England, assisted by OWEN E. MOTT, PH.D. (Heidelberg), Demonstrator of Chemistry, Municipal Technical College, Derby, England. With the co-operation of the Author. First Edition, First Thousand. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1903. pp. xvii + 555. Price, $2.50.

The author gives in his preface some of his reasons for writing this book: "Most of the short text-books of organic chemistry contain a great number of isolated facts. The number of compounds described in them is so considerable as to confuse the beginner. Moreover, the theoretical grounds on which the division of the science is based are often kept in the background; for example, the proofs given of the constitutional formula frequently leave much to be desired. However useful their books may be for reference, they are often ill-suited for text-books, as many students have learned from their own experience.

"In this book I have endeavored to keep the number of unconnected facts within as narrow limits as possible and to give prominence to the theory underlying the subject. For this reason a proof of the structure of most of the compounds is given." * * * "The book is essentially a text-book, and makes no claim to be a "Beilstein" in a very compressed form."

The book undoubtedly has much to recommend it. It is clearly written and the subject is treated in a thoroughly scientific way and yet not pedantically. It is not so thoroughly scientific as to be uninteresting.

The general arrangement is much like that commonly adopted. The division into "The Fatty Compounds" and "The Aromatic Compounds and Substances Related to Them" is retained, and the classification of compounds under these heads makes no claim to originality.

While the translation, on the whole, is smooth, there are some passages that will give trouble. On page 391 occurs this statement: "It has been proved that no isomers of ketoximes, $\begin{matrix} R \\ \diagdown \\ R' \diagup \end{matrix}\!\!>\!C : NOH$, exist, when R and R′ are similar, two isomers are known when these groups are dissimilar." This is not clear nor is it true. It is true, however, that when R=R′, when R and R′ are the same (not similar), no isomers exist.

Again, on page 101, the following is given as the proof that "the acids $C_nH_{2n}O_2$ contain the group $-C\overset{O}{\underset{OH}{<}}$ linked to an alkyl-radicle": "It was stated in 82 that a solution of sodium-alkyl in zinc-alkyl is obtained when sodium reacts with the latter. When a stream of dry carbon dioxide is passed into this solution there is formed the sodium salt of an acid which contains 1 carbon atom in the molecule more than the alkyl group. Thus, sodium methyl, CH_3Na, yields sodium acetate, $C_2H_3O_2Na$. This reaction may be explained by assuming that the sodium atom is released from the alkyl group and reacts with CO_2 becoming linked to one of its oxygen atoms, for which it possesses great affinity. In this way $C\overset{O}{\underset{O}{<}}$ is converted into $-C\overset{O}{\underset{ONa}{<}}$. Since this group, and also the alkyl-radicle from which the sodium atom has been separated have only one free carbon bond apiece it may be assumed that the two groups unite, forming a compound

$$C_nH_{2n+1}-C\overset{O}{\underset{ONa}{<}}."$$

The reviewer is of the opinion that the beginner will worry over this a good deal. The lack of clearness in this case cannot be laid at the door of the translator alone. The author is partly responsible. The translator is not always consistent in the writing of names of compounds. A glaring case of inconsistency is to be found on page 116. The names of three esters are there given within the limits of three lines and they are printed thus: "isoamyl-valerate," "ethyl butyrate," and "isoamylacetate." This is confusing to the student and does not help him to overcome the slovenly habits with which he is usually endowed by nature.

The name "Brühl" is incorrectly given "Bruhl" on page 301.

In regard to the formula of benzene, the author gives the preference to the centric formula first proposed by Armstrong and afterwards adopted, for a time, by Baeyer. As Baeyer's work on the constitution of benzene advanced, however, he gave up the centric formula of Armstrong and expressed himself as in favor of the diagonal formula of Claus. The latest utterance of Baeyer on this subject justifies the belief that he still prefers the Claus formula to all others.

On page 78 the author says the word mercaptan is derived

from *corpus mercurio aptum*. This is a mistake. Mercaptan is derived from *corpus mercurium captans*. Zeise gave the name mercaptum to the radical C_2H_5S, of which, with hydrogen, he held mercaptan to be made up $H + C_2H_5S$. The word mercaptum was derived from *corpus mercurio aptum* [see Zeise, Ann. chim. phys., (2), **56**, 87 (1834)].

In brief, the book, like others, is not free from errors. Those that have been detected are not, however, serious, and they do not materially detract from the value of the book.

I. R.

PAPERS ON ETHERIFICATION AND ON THE CONSTITUTION OF SALTS. By ALEXANDER WILLIAMSON, LL.D., F.R.S. (1850–1856). Edinburgh: The Alembic Club; Chicago: The University of Chicago Press. 1902. Price, 40 cents.

The Alembic Club reprints are well known to chemists. This is the sixteenth issue. All the volumes thus far published are of fundamental importance, including, as they do, papers by Black, Dalton, Wollaston, Cavendish, Avogadro, Davy, Scheele, and other fathers of the science. Students of chemistry, young and old, are advised to buy every one of these volumes and read them over and over again. By an arrangement with the Alembic Club, they can now be obtained from the University of Chicago Press for a small price.

I. R.

A TEXT-BOOK OF VOLUMETRIC ANALYSIS. With special reference to the volumetric processes of the pharmacopoeia of the United States. Designed for the use of Pharmacists and Pharmaceutical Students. By HENRY W. SCHIMPF, Professor of Inorganic Chemistry in the Brooklyn College of Pharmacy. Fourth Edition, Revised and Enlarged. New York: John Wiley & Sons. 1903. pp. xxix + 553.

The third edition of this book was reviewed in this JOURNAL (**21**, 98). The present issue differs principally from the previous one by containing additional methods for the volumetric analysis of alkaloids. What was said in the previous review of the general character of the book applies at the present time with added force. One is more than ever impressed with the mechanical nature of the instructions and of the non-convincing character of the directions. Throughout the book the personal element, which plays so important a part in the successful text-book, appears to be lacking and it appears as a mere undigested compilation, for the most part badly expressed. That there has been a demand for a book of this kind, however, is evidenced by the fact that it has reached its fourth edition.

H. F.

DIE ALUMINIUM INDUSTRIE. Von DR. F. WINTELER. Braunschweig: Friedrich Vieweg und Sohn. 1903. pp. xi + 108. Price, 6 marks.

This is one of those useful pamphlets which the Germans

know so well how to prepare. To those wishing to get a survey of the aluminium industry without searching through a mass of details in special treatises, or looking through the journals for the original articles, this book will be very valuable. It treats of the early history of the metal, its chemical and physical properties, the preparation of pure alumina from bauxite and kaolin, carbon electrodes, electric furnaces, the measurement of electric currents, the working of the metal and its uses.

While none of the chapters will serve as a complete guide, and specialists will complain because their particular field has been slighted, nevertheless much information has been condensed into the volume. It is indeed a very useful review of the patent and scientific literature of the aluminium industry. Incidentally, the author gives methods of analysis of bauxite, clay, cryolite, and commercial aluminium. H. F.

ELEMENTS OF INORGANIC CHEMISTRY. By HARRY C. JONES, Associate Professor of Chemistry in the Johns Hopkins University. New York: The Macmillan Co. 1900. pp. 326.

The sympathies of every thoughtful, conscientious teacher must needs go out to the author who ventures to give us a new "Elements of Inorganic Chemistry." All will admit there is an abundance of material for such a book and an opportunity is not wanting, but the question is, *what* and *how much* to present?

The fact that these questions have never been answered satisfactorily, together with the fact that every writer sees in ordinary chemical phenomena the chance to apply the pet theories of that particular branch of the science in which he himself is most interested, doubtless accounts for the ever increasing number of such publications.

In the book before us the attempt has been made to present the simpler aspects of chemical change from the standpoint of our more recent acquisitions in the domain of physical chemistry. To the author this point of view is the natural and normal one, and from his standpoint this is the normal and natural method of presenting the subject of chemistry to the mind of the young student. Whether it is the best method of presenting the subject of elementary chemistry, time and the experience of good teachers can alone decide. In the main, the original conception of the book has been well carried out and carefully executed. For a work of its kind, it contains much that is new and refreshing, and of necessity a good deal that is old. The plan of putting directions for experiments at the conclusion of each of the several topics treated of, so as to

not interfere with continuity in the presentation of the subject, must commend itself to student and instructor alike. A full and complete index also is not the least valuable of its many excellent features, and in mechanical execution it leaves but little to be desired.

In our opinion, however, not only is nothing gained, but something is distinctly lost, by presenting the physical properties of a substance at the close of each substance considered, as has usually been done.

Ordinarily, there is nothing included under this head that is not readily intelligible to the student as a quality or characteristic of the substance under consideration, and the arrangement adopted only serves needlessly to accentuate physical and chemical differences which in reality are intimately correlated. In our opinion this mode of presentation is not in harmony with the true spirit of physical chemistry.

J. H. K.

A Laboratory Guide to Qualitative Analysis with the Blowpipe. By F. W. Martin, Ph.D. New York: John Wiley & Sons. 1903. pp. iv + 47.

After reading the author's preface one is left in doubt as to the class of readers for whom the book is intended since he says "this little volume is designed to be used, primarily, as a laboratory guide by students of qualitative analysis; secondarily, as a work of reference by practising chemists;" and later he writes, "this book is intended for the use of teachers who have a comprehensive knowledge of chemical facts and phenomena."

If the book be placed in the hands of the student of qualitative analysis without the supervision of a teacher with "comprehensive knowledge of chemical facts" its value is open to question, but if supplemented with explanations from the instructor it will prove a valuable adjunct to the usual course in wet methods. The author's attempt to bring dry methods to the attention of the teacher of qualitative analysis is certainly worthy of praise.

The use of such hybrids as "basigen" and "acidigen" is most unfortunate; on p. 24 we read that "the bead has its surface *eaten* away by dilute acid" and that the "products of these *by-reactions* separate as minute crystals." It is questionable whether this book will find its way into the libraries of many practising chemists since all that it contains is to be found in larger and more complete works on blowpipe analysis.

As a companion to a text-book on qualitative analysis, however, this little work will surely find its place. F. H. G.